Experimental and Computational Studies on Copper and Hydrobenzoin Derivatives in Catalytic Asymmetric Reactions

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Contents

List of Figures

List of Schemes

List of Tables

1 Abstract

The use of theory to understand and facilitate catalytic enantioselective organic transformations involving copper and hydrobenzoin derivatives is reported. Section A details the use of theory to predict, facilitate, and understand a copper promoted aminooxygenation reaction reported by Chemler et al. Using Density Functional Theory (DFT), employing the hybrid B3LYP functional and a LanL2DZ/6-31G(d) basis set, the mechanistic details were studied on a *N*-tosyl-*o*-allylaniline and a α-methyl-γ-alkenyl sulfonamide substrate. The results suggest the N-C bond formation proceeds via a cis-aminocupration, and not through a radical-type mechanism. Additionally, the origin of diastereoselection observed with α-methyl-γ-alkenyl sulfonamide arises from avoidance of unfavourable steric interactions between the methyl substituent and the *N*-protecting group. Section B details the computationally guided, experimental investigation of two hydrobenzoin derivatives as ligands/catalysts, as well as the attempted synthesis of a third hydrobenzoin derivative. The *bis*-boronic acid derived from hydrobenzoin was successful as a Lewis acid catalyst in the Bignielli reaction and the Conia ene reaction, but provided only racemic products. The chiral diol derived from hydrobenzoin successfully increased the rate of the addition of diethyl zinc to benzaldehyde in the presence of titanium tetraisopropoxide, however poor enantioinduction was obseverved. Notably, the observed reactivity was successfully predicted by theoretical calculations.

2 Acknowledgements

First and foremost I have to thank my parents whom have stood by and supported me my entire life. Although I am sure you would have sooner thought I would end up in prison than grad school, you stood by me none the less, and now here I am. Margo and Jackie, you are the best siblings I could ask for. Dr. Dudding, over the past five years you have been an excellent mentor and a good friend. Your enthusiasm for chemistry and science in general is nothing short of infectious. To the members of the Dudding group, past and present, you have all been a pleasure to work with and I have enjoyed and benefited from our countless discussions. I wish you all the best. Egor, your limitless knowledge continues to astound me. Dr. Britton, thank you for all of your time and help, and your willingness to partake in this collaboration. Your outlook on life and chemistry is truly refreshing and encouraging. To the Britton group, you are all fantastic people and outstanding chemists. I have learned an enormous amount from all of you, and am a better person for having known you all. Jeffery Mowat, you taught me much about chemistry and beer, I owe you many thanks. I would like to thank the members of my committee, Dr. Hudlicky and Dr. Rothstein. I have learned an enormous amount from you in terms of both scientific information and integrity, and I have nothing but the utmost respect for both of you. Lastly, I would like to thank professor Moitessier for your role as my external examiner, your comments and insight were very helpful and greatly appreciated.

3 Introduction

The term "*chirality*" is derived from the Greek word for hand, "*kheir*". The term was introduced because our hands, being non-superimposable mirror images of one another, are perhaps the most recognizable chiral objects known to man. However, as every chemist and biologist is well aware, the underlying significance of chirality is far more fundamental. Within the field of organic synthesis, the importance of chirality and the necessity for asymmetric chemical transformations is well asserted.[1] This is apparent from the countless publucations demonstrating the control of asymmetry in a reaction. Many different approaches have been developed for this purpose, including the use of starting materials taken from the natural chiral pool, separation of chiral racemic compounds, chiral auxiliaries, enzymatic transformations, and kinetic resolution. Another method with significant potential is asymmetric catalysis. The principle behind asymmetric catalysis is that a chiral molecule can selectively promote the conversion of an achiral substrate to a single chiral product, at which time it is regenerated, allowing it to promote further transformations. As such, only sub-stoichiometric quantities of the chiral catalyst are required, ultimately leading to a reaction that requires less extreme conditions, is more environmentally friendly, and is more economically viable. Two important and well-known examples include catalytic asymmetric hydrogenation and dihydroxylation, which have proven to be invaluable to the synthetic community. Other important examples of catalytic asymmetric reactions include the Takasago Process, for the manufacturing of (-)-Menthol[2,3]

and the Sharpless catalytic asymmetric epoxidation.[4] The challange in developing a desired catalytic asymmetric process is often associated with obtaining the desired selectivity. If a catalytic asymmetric reaction is sufficiently optimized, only a single stereoisomer will be produced. For this to occur, the transition state leading to the desired stereoisomer must be sufficiently lower in energy than those leading to the undesired stereoisomer(s). For this reason, it is important to understand the factors which influence transition state energies. Often a reported catalytic asymmetric methodology is far too substrate specific, and subtle variations in substrate structure result in dramatically decreased yield and/or selectivity. Moreover, substantial time and resources are commonly spent on ligand, catalyst, solvent, and other modifications/optimization. It is for this reason that a computational approach to asymmetric catalysis may prove beneficial, and the incorporation of computational chemistry into the development, understanding, and optimization of catalytic asymmetric processes might facilitate further success in this field.

Recent decades have served witness to the rapid evolution of computational organic chemistry. Our understanding of reaction mechanisms and chemical properties has greatly benefited from theoretical descriptions of molecular interactions. However, despite the notable accomplishments in the field of computational organic chemistry, there exists a far greater potential. There will likely become a time when reactions will be optimized *in silico*, at whic time the experimental synthesis will be performed with ease. To reach this seemingly distant goal, we must first continue to advance the field of computational organic chemistry. Many different theoretical foundations have

been developed for the purpose of studying chemical systems computationally, including molecular mechanics, density functional theory (DFT), Hartree-Fock (HF) and post Hartree-Fock *ab-initio* calculations, molecular dynamics, Monte-Carlo, and quantum Monte-Carlo. The use of computational chemistry as a tool to understand reaction mechanisms has been around for over thirty years.[5,6] While the application of computational chemistry to facilitate optimization and understanding of catalytic reactions began over a decade and a half ago,[7] the first report of a computationally investigated organocatalytic reaction was in 2001 by Houk and Bahmanyar.[8] This investigation of the Hajos-Parrish reaction (an L-proline catalyzed intramolecular aldol reaction) was instrumental in setting the stage for studying and predicting catalytic reactions with computational chemistry. Computational chemistry has now proven itself to be valuable in understanding and predicting chemical properties and reactivity. Various reports have been published where computations have been used to predict/explain the outcome of chemical reactions and provide valuable insight into a given catalytic asymmetric process.[9–12] Moreover, computational models are also used in the discipline of biochemistry as a tool to understand enzyme mediated processes.[13–16] Despite these achievements, computational chemistry is in its relative infancy and has its own unique set of hurdles to overcome. In theory, it should be capable of *in silico* optimization of chemical reactions. In order to attain this ideal objective, it is important to continue the application and examination of such research. It is in this light that the current research was pursued. By applying the latest methods and technologies in computational chemistry to synthetic transformations, we in-

crease our fundamental understanding of these reactions, while simultaneously advancing the science of computational chemistry. Presumably, this will create a self-consistent cycle of improvements in these two fundamentally important areas of science. The research herein describes the use of computational chemistry to help investigate specific examples of catalytic asymmetric reactions.

4 Section A - Organocopper Catalyzed Asymmetric Reactions

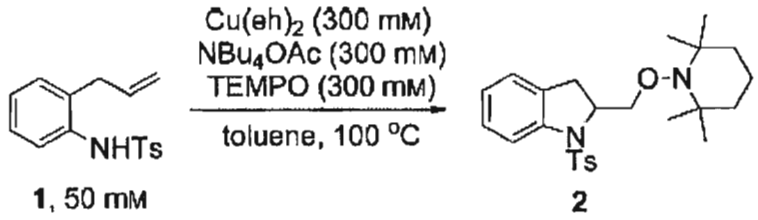
4.1 Background/Introduction (Section A)

In terms of an ideal metal for asymmetric catalysis, copper benefits from being cheap, abundant, and easy to handle. Copper has proven very useful in transition metal catalysis for quite some time and the *copper catalyst toolbox*[17] has become quite large. The utility of copper is apparent from the Ullmann,[18] Cadiot-Chodkiewicz,[19] and Sonogashira couplings,[20] as well as from the Gilman reagent,[21] the Goldberg condensation,[22] and the Hurtley reaction.[23] The increasing reports of copper mediating useful organic, as well as bioorganic, transformations has prompted in-depth mechanistic studies to elucidate its role.

Alkene difunctionalization reactions are important in organic synthesis and the discovery and development of copper-catalyzed and promoted difunctionalizations of alkenes is a burgeoning area of chemical research.[24–26] The alkene functional group is ubiquitous, the resulting products are useful, and copper is a versatile and relatively inexpensive reagent and catalyst. A number of mechanistic pathways and intermediates are feasible, and the precise pathway depends on the copper oxidation state (Cu(0), Cu(I), Cu(II), or Cu(III)) and the reaction components.[27] Copper can serve as a Lewis acid, a p-acid, and an oxidant, and is known to promote reactions through organometallic as well as redox mechanisms. Recently, a copper promoted aminooxygena-

tion has been described in the literature[28] yet many questions surrounding its mechanism, and the nature of the active species involved still remained. Considerable experimental data had been reported, and mechanistic studies were underway which would be well served by a theoretical description. As such, a computational investigation was initiated to shed light on the finer details of this coper catalyzed aminooxygenation (Scheme 1).

Scheme 1: Aminoxygenation Reaction of *N*-tosyl-*o*-allylaniline



1, 50 mM **2**

4.2 Computational methods

To investigate the aminocupration mechanism we carried out calculations at the Kohn-Sham hybrid-DFT B3LYP[29] level of theory using the Gaussian 09 and GaussView v5.0.8 programs.[30] The GenECP method was employed with a 6-31G(d) basis set applied to all atoms (*i.e.* H, C, N, O, S) except copper, which was computed using the Los Alamos LAN2DZ[31–33] basis set. This combination was applied because the sole use of the 6-31G(d) basis set resulted in exaggerated basis set superposition error (BSSE), while sole use of the LanL2DZ basis set did not properly account for the hypervalent nature of sulfur. The origin of the exaggerated BSSE is readily interpreted in the context of the C-Cu homolysis step of the reaction sequence. The dissociation

of copper in the form of C-Cu bond cleavage gives rise to two separate species, one with copper, and one without. Before the C-Cu bond cleavage occurs, the electrons from all atoms have available to them (to some extent) the entire set of orbitals associated with Copper. However, upon dissociation, some electrons no longer have access to those orbitals. In the context of the 6-31G(d) basis set, the result is a loss of the d orbitals which are present exclusively because of the copper atom. Thus, the electons in the fragment not containing copper have a decreased effective basis set relative to both the associated complex and the other dissociated fragment. Further compounding this issue is the fact that the Cu atom is directly involved in bond homolysis. In order to circumvent this issue, the LanL2DZ basis set was chosen to accurately represent the electronic structure of copper, without producing this exaggerated BSSE upon dissociation. The LanL2DZ basis set did succeed in this respect, however, as a consequence of using the Ne core as an effective core for all elements between Ne and Ar, and restricting access to the unoccupied d orbitals, the basis set did not accurately describe the hypervalent nature of the sulfur atom. In accordance with these findings, we used the GenECP keyword in Gaussian and used both basis sets as stated above. The use of this method has precedence in the realm of computing Cu promoted reactions.[34,35]

In order to decrease computational cost and reduce conformational space, $Cu(OAc)_2$ was used instead of $Cu(eh)_2$. This was thought to be a reasonable truncation as experiments had shown that ethyl hexanoate was only necessary to increase the solubility of the Cu species, and it was unlikely that increasing the alkyl chain length of the ligand would have had any significant electronic

effects, if any at all. An implicit solvation model to account for solvent effects was neglected because of the large increase in the time required to complete the computations relative to the change in energetic trends. Neglecting solvent effects in our model is largely a reasonable simplification due to the low dielectric constant of the utilized solvent (toluene, $\epsilon = 2.38$) and our use of relative, rather than absolute, energies for comparison of mechanistic scenarios. Introduction of error from this simplification would have the greatest impact on species with a large charge separation. It is noteworthy that previous computational studies involving copper complexes and C-Cu bond dissociation energies have shown that the observed results of gas phase DFT calculations using the B3LYP functional were consistent with experimental findings.[36–39] In general, the solvent stabilizes charged species, or systems where the charge is separated/polarized. We use the calculations to compare various pathways via relative energies. All of the complexes we have examined, except for one, have an overall charge of zero and similar degrees of charge separation throughout.

Thus, we would expect solvation to lower all energies by similar amounts, resulting in little to no significant change in relative energies between steps. Nevertheless, in order to gauge the effect that toluene would have on our computed B3LYP/GenECP gas phase findings, we carried out as a case example the geometry optimizations of the three key stationary points **GS-A**, **TS-A** and **I-1A** in toluene using the IEFPCM solvation model with the keyword added [scrf=smd]. These three points correspond to the ground state, aminocupration transition state, and subsequent intermediate of pathway A. It was found that the activation barrier to aminocupration in this series was

unchanged to the first decimal place (17.2 kcal/mol) while the subsequent intermediate **I-1A** was lowered in energy by 2.2 kcal/mol. This latter energy change could result in a slightly endothermic rather than exothermic subsequent C-Cu bond homolysis, but the overall message of the calculations remains unchanged.

4.3 *N*-tosyl-*o*-allylaniline

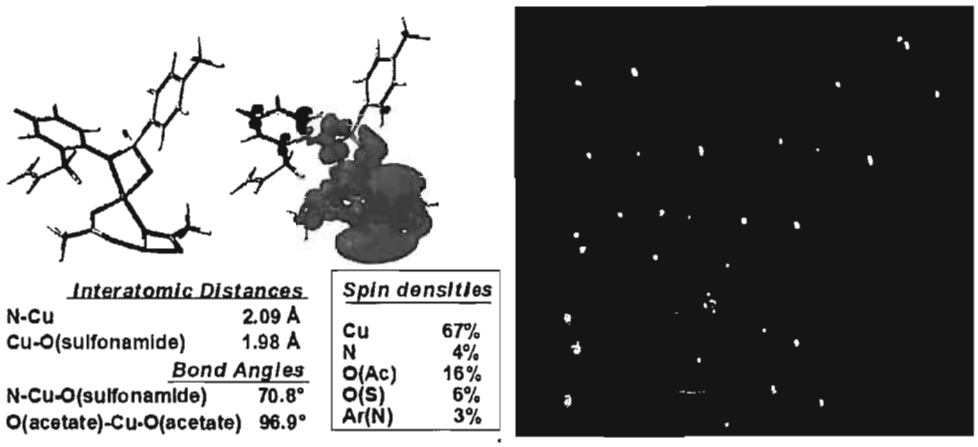
The ground state geometries of three [R_2N-Cu] complexes derived from complexation of *N*-tosyl-*o*-allylaniline (**1**) with $Cu(OAc)_2$ were calculated at 25 °C, and a spin density analysis was performed on each resulting structure (Figures 1, 3, and 2). These complexes differ in the number of acetate ligands on the copper(II) center, and the cation counterion. The first two complexes are those potentially formed from combination of the lithium amide of **1** with $Cu(OAc)_2$ (as in the reported EPR experiment[40]), [Ts(2-allylphenyl)N-$Cu(OAc)_2$]Li (**GS-Li**) and [Ts(2-allylphenyl)N-Cu(OAc)] (**GS-B**). The third complex is [Ts(2-allylphenyl)N-Cu(OAc)(HOAc)] (**GS-A**), a structure that may most closely resemble the intermediate formed under the reaction conditions involving Bu_4NOAc. These complexes all have distorted square planar Cu coordination. In all three structures, the sulfonamide oxygen also coordinates to the Cu(II) center, indicating the sulfonamide favors bidentate coordination. AIM analyses[41,42] were performed on the three ground state structures (Figures 1, 3, and 2). In each, a bond critical point (3,-1) was located between the sulfonamide oxygen and Cu, which is indicative of the existence of a bond.

Furthermore, a ring critical point (3,+1) was present in each ground state structure at the center of the Cu-O-S-N ring. A (3, -1) bond critical point is defined as a saddle point of electron density. In three dimensional space, the electron density decreases in both directions along the axes of two dimensions, and increases in both directions along the axis in the third dimension. A (3, +1) ring critical point is also a saddle point of electron density, however the electron density increases in both directions along the axes of two dimensions, and decreases in both directions along the axis in the third dimension.

Tetrahedral twist is a description of the degree from which the coordination sphere deviates from square planarity.[43] The tetrahedral twist of the calculated **GS-Li** complex is 4.5°. More dramatically, the bond angles of this complex deviate from the ideal 90° by 5.1° to 19.2° [*e.g.* the N-Cu-O(sulfonamide) bond angle is 70.8°]. The tetrahedral twist of the calculated **GS-B** complex is also 4.5°. The bond angles also deviate from 90° by 19.3° to 24.1° in this complex [e.g. the N-Cu-O (sulfonamide) bond angle is 72.0° and the OAc-Cu-OAc bond angle is 65.9°]. These deviations from ideal square planarity might cause significant orbital distortion resulting in the loss of the g-parallel signal in the EPR spectra.

Spin density analysis revealed the majority of the spin resides on Cu. For **GS-Li**, 67% of the spin density resides on Cu while a total of 12% of the spin density resides on the sulfonamide ligand (delocalized through the N, Ar and SO_2). In **GS-B**, 53% of the spin density resides on Cu and 26% spin density is delocalized through the sulfonamide ligand. The remaining spin density is

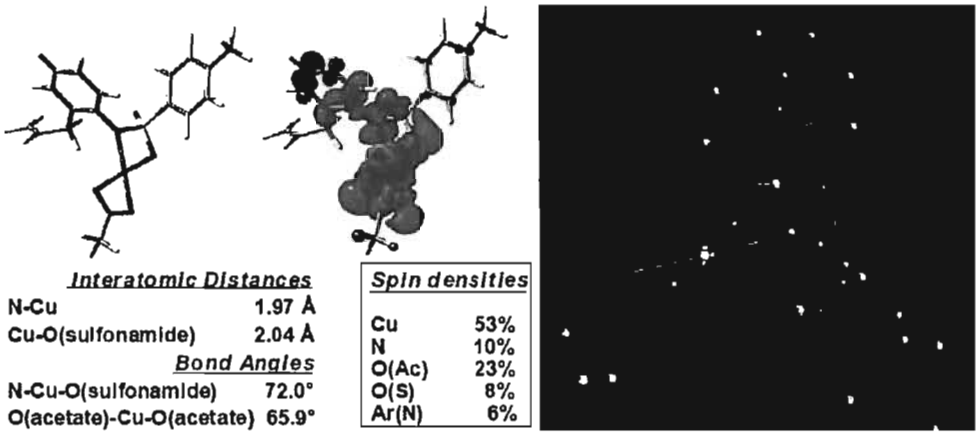
Figure 1: Ground State Spin Density Analysis of [OAc_2N-Cu]Li (**GS-Li**)



Interatomic Distances	
N-Cu	2.09 Å
Cu-O(sulfonamide)	1.98 Å
Bond Angles	
N-Cu-O(sulfonamide)	70.8°
O(acetate)-Cu-O(acetate)	96.9°

Spin densities	
Cu	67%
N	4%
O(Ac)	16%
O(S)	6%
Ar(N)	3%

Figure 2: Ground State Spin Density Analysis of [OAcN-Cu] (**GS-B**)

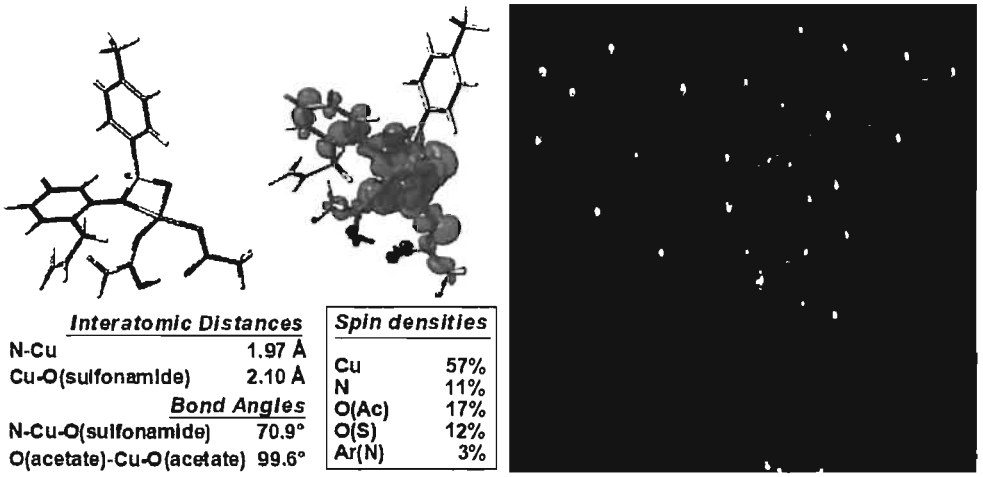


Interatomic Distances	
N-Cu	1.97 Å
Cu-O(sulfonamide)	2.04 Å
Bond Angles	
N-Cu-O(sulfonamide)	72.0°
O(acetate)-Cu-O(acetate)	65.9°

Spin densities	
Cu	53%
N	10%
O(Ac)	23%
O(S)	8%
Ar(N)	6%

delocalized onto the acetate ligands. This indicates a significant degree of spin delocalization onto the sulfonamide ligand, but the majority still resides on Cu. This analysis is not only consistent with the EPR spectra observed for the [R_2N-Cu] intermediate, but the EPR spectra was indecipherable before the ground states and associated spin densities were calculated. Since the spin density on the nitrogen ligand is delocalized, with only 3.5-9.6% located on N, the N-Cu superhyperfine coupling would be expected to be small, which

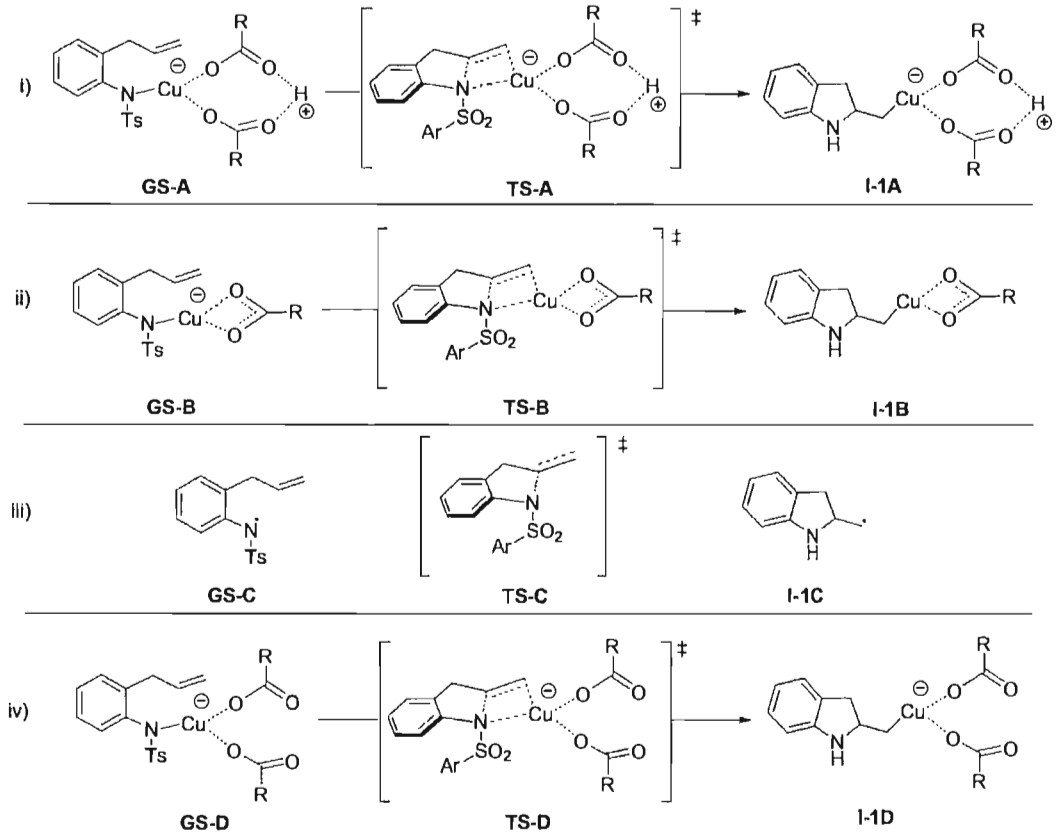
Figure 3: Ground State Spin Density Analysis of [HOAc(OAc)N-Cu] (**GS-A**)



it was. Similar to the other two complexes, spin density calculations on the ground state structure of **GS-A** indicate that Cu retains the majority of the spin density (57%) and the sulfonamide ligand contains 27% total spin density.

Four mechanistic pathways were considered for the $Cu(OAc)_2/Bu_4NOAc$-promoted aminooxygenation reaction of *N*-tosyl-*o*-allylaniline, **1** (Scheme 2, *i-iv*). Pathway A begins from the ground state N-Cu complex **GS-A** and is aptly named the neutral, two-acetate pathway. Pathway B begins from the N-Cu ground state complex **GS-B** and is named the neutral, one acetate pathway. Pathway C also begins with the ground state N-Cu complex **GS-A**, but is then followed by N-Cu homolysis resulting in an aminyl radical which undergoes direct N-C bond formation. Accordingly, pathway C is named the radical pathway. Pathway D begins with the ground state N-Cu complex **GS-D**, $[(R^1R^2N)Cu(OAc)_2]^-$, and is therefore referred to as the anionic, two ligand pathway.

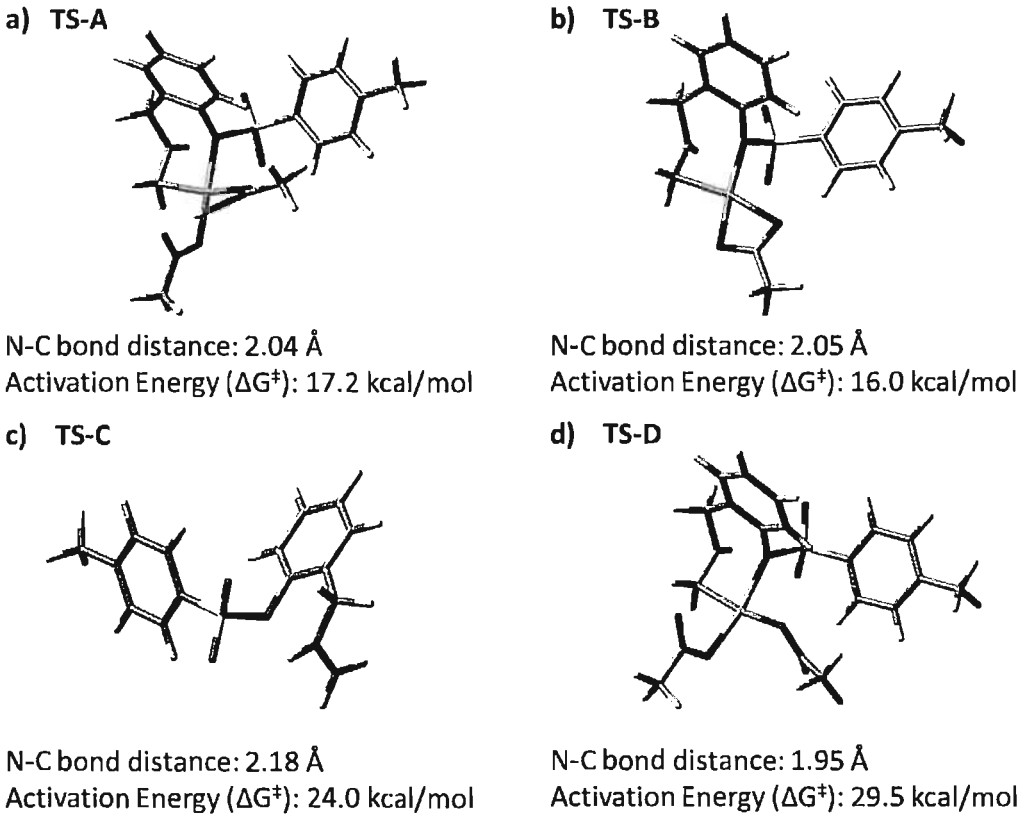
Scheme 2: Mechanistic alternatives for the copper(II)-promoted alkene aminoxygenation of *N*-tosyl-*o*-allylaniline.



These four mechanistic scenarios were calculated at 110°C, and the optimized transition states were confirmed to be first-order saddle points by the appearance of a single imaginary frequency. Furthermore, the respective product complexes immediately following from the transition states were located using the intrinsic reaction coordinate (IRC) method[44,45] and confirmed to be minima by the appearance of only real vibrational modes. Thereafter, each intermediate shown was located by optimization to the lowest energy minima for the corresponding geometry.

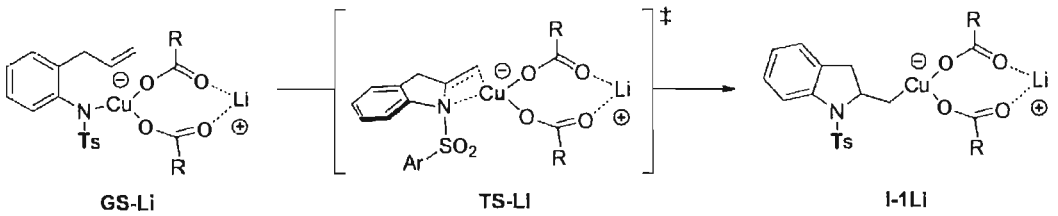
The calculated aminocupration transition states and activation barriers for pathways A through D are shown in Figure 4. These results indicated that pathways A and B were the most likely mechanistic candidates. We found

Figure 4: Calculated aminocupration transition states for mechanisms A-D



that the one-acetate-ligand mechanism, path B, has a lower aminocupration activation barrier than the two-acetate neutral mechanism, path A, by about 1.2 kcal/mol. Interestingly, kinetics experiments indicated a half-fold decrease in reaction rate when the base was changed from Bu_4NOAc to *n*-BuLi. We thus calculated the aminocupration activation barrier starting from the ground state complex **GS-Li** (Figure 5). In doing so, we found it was 2.8 kcal/mol

Figure 5: Aminocupration proceeding with two ligands and a Li counterion



higher than the activation barrier for transition state A, path A, at 100°C (the temperature the kinetics experiments were run at). This is consistent with experimental findings that the reaction involving **1** deprotonated with nBuLi is half the rate of the reaction involving **1** and Bu_4NOAc (*vide supra*). Additionally, the fact that there is a difference in rate between the two series indicates that the copper centers in each intermediate are not likely to lose an acetate ligand to form intermediate I-1B (pathway B), since then the rates would be expected to be the same.

Nevertheless, the aminooxygenation reaction mechanisms of pathway A and B were modelled in full (Figure 6). A schematic representing pathway A is shown in Scheme 3.

Scheme 3: 2 ligand neutral pathway A

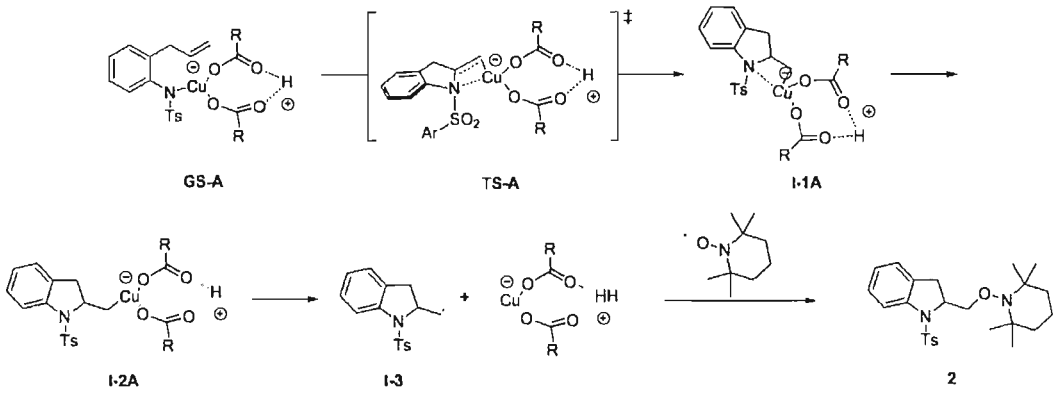
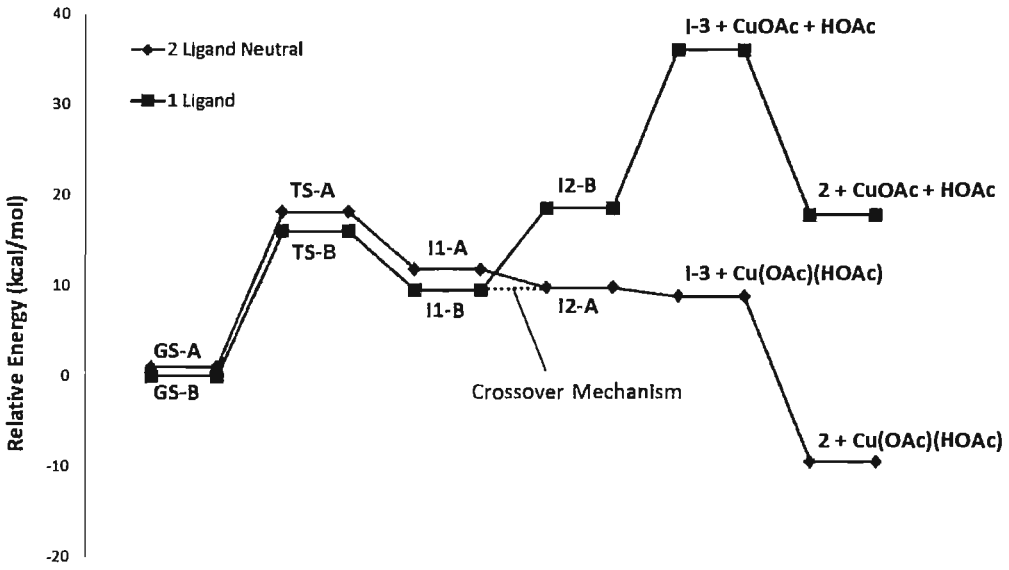


Figure 6: Comparison of free energies for pathways A and B



Upon detailed investigation of reaction coordinates A and B (Figure 6), a dramatic ligand effect is observed. The most stable aminocopper intermediate to emerge from **TS-B** is **I-1B**, which still maintains N-Cu coordination. Loss of this coordination and homolysis to carbon radical **I-3** and CuOAc resulted in a 26.5 kcal/mol higher energy state. The majority of the energy cost appears to be loss of the C-Cu bond (17.5 kcal/mol), but loss of the N-Cu bond is also endothermic (9.0 kcal/mol). The organocopper intermediate emerging from **TS-A** is **I-1A**, which also maintains N-Cu coordination. Loss of N-Cu coordination generates a re-oriented, minimized C-Cu intermediate, **I-2A**, which has an acetate and HOAc ligand bound to it. In the path A series, the re-oriented intermediate **I-2A** is actually lower in energy than **I-1A** by 2.0 kcal/mol. The different relative change in energy between the two C-Cu intermediates in the two series might be explained by the formal

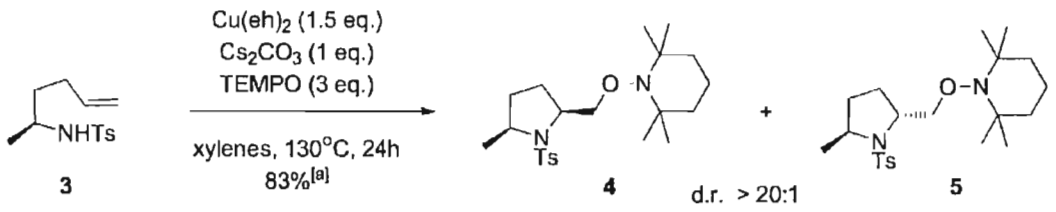
charge on Cu. In series A, **I-1A** has a Cu with a formal charge of +2, so when it releases the N ligand, it becomes Cu with a formal charge of +1, and this change in formal charge on Cu is apparently favorable even though the Cu becomes tricoordinate in going to **I-2A**. In series B, **I-1B** has a formal charge of +1, so when it releases the N ligand to yield **I-2B**, it becomes Cu with formal charge of 0. This is apparently not as beneficial a change compared to becoming the tricoordinate C-Cu intermediate **I-2B** (the acetate is bidentate), so **I-1B** to **I-2B** is an endothermic process. Homolysis of **I-2A** to give the carbon radical **I-3** and Cu(HOAc) is exothermic, but by only 1.0 kcal/mol (it is possible this step is actually slightly endothermic if solvation is taken into account, see previous discussion on solvation). Trapping of the carbon radicals with TEMPO was found to be highly exothermic, resulting in the optimized aminooxygenation product **2** and the respective Cu(I) salt. The large difference in product energies between pathways A and B is the result of the copper(I) species, Cu(OAc) + HOAc in the one-acetate-ligand pathway B, and Cu(OAc) - (HOAc) for the two-acetate-ligand pathway A. Thus, it appears that ligation of the second acetate greatly stabilizes the Cu(I) homolysis product, thereby impacting the overall reaction profile. It is thus proposed that the two-acetate-ligand (neutral) mechanism (pathway A) is overall lower in energy and thus a reasonable mechanism. Another mechanistic possibility, however, would be a cross-over mechanism in which aminocupration proceeds through the one-acetate-ligand pathway (pathway B) resulting in the [C-Cu] complex **I-1B**, which then picks up an acetate (as HOAc to maintain overall neutrality) to generate intermediate **I-2A**. At this point, the two-ligand,

neutral mechanism (pathway A) is embarked upon whereby C-Cu homolysis is followed by capture of the resulting carbon radical **I-3** by TEMPO to yield the exothermic aminooxygeantion product **2** and the respective Cu(OAc)(HOAc) salt. Bond dissociation energies were used in this analysis because the C-Cu homolysis transition states were difficult and in most cases impossible to locate.[36,37] The calculated aminocupration transition states all possess distorted square-planar copper geometries (Figure 4). Spin density analysis of transition states **TS-A** and **TS-B** indicate the majority of spin density resides on Cu and little increase in nitrogen spin from ground state to transition state is observed. The spin on nitrogen never exceeds 15% and thus the nitrogen does not possess significant radical character. Wiberg bond indices[46,46–49] were analyzed to quantify the extent to which the N-C and Cu-C bonds are formed at the transition states. Accordingly, the Cu-C bond is 73% formed in **TS-A**, while the N-C bond is only 49% formed. Similarly, the Cu-C bond is 71% formed at **TS-B**, while the N-C bond is only 49% formed. This indicates the alkene amincupration is being led by Cu p-bond activation. In the most stable C-Cu intermediates, **I-2A** and **I-1B**, significant spin density, 40% and 36%, respectively, resides on the terminal carbon, which leads to the prediction that this carbon will behave like a radical, which it subsequently does.

4.4 α-Methyl-pyrrolidine

The $Cu(eh)_2$ promoted aminooxygenation reaction of α-methyl-γ-alkenyl sulfonamide **3** occurred in about 83% yield and greater than 20:1 *cis*/*trans*

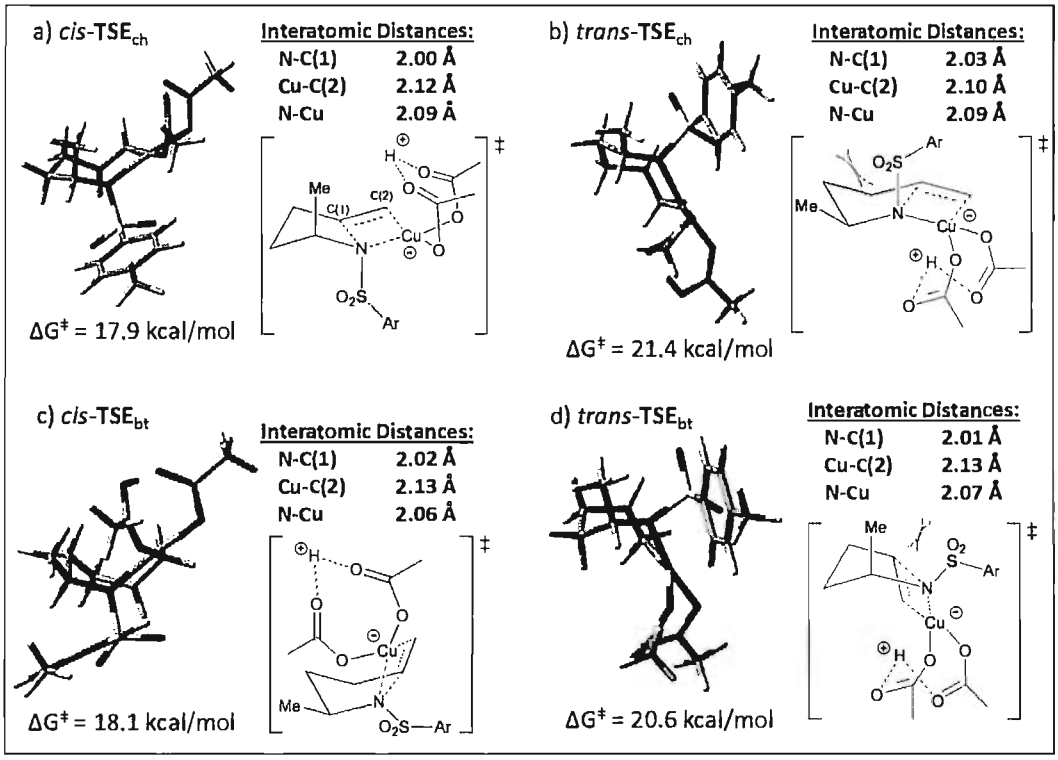
Scheme 4: Aminooxygenation reaction of α-methyl-γ-alkenyl sulfonamide



[a] 81% yield and d.r. >20:1 with Bu_4NOAc (1 eq.) in place of Cs_2CO_3

diastereoselectivity irrespective of whether Cs_2CO_3 or Bu_4NOAc was used (Scheme 4). This 2,5-*cis*-selectivity is consistent for a number of substrates. We thus continued our computational investigation to this reaction set in order to understand the origin of this stereoselectivity. From studying the aminocupration of *N*-tosyl-*o*-allylaniline we were confident that the active species is that of the two ligand neutral pathway, or the one ligand pathway. We therefore calculated eight possible aminocupration transition states for this reaction, four for each pathway that lead to the observed 2,5-*cis*-pyrrolidine **4**, and four for each pathway that lead to the 2,5-trans-pyrrolidine **5**. The four potential aminocupration transition states for the two-ligand neutral pathway E are shown in Figure 7 . Transition states *cis*-**TS-E**$_{ch}$ and cis-**TS-E**$_{bt}$ (ch = chair, bt = boat) are favored (lower in energy by at least 2.5 kcal/mol) due to minimized steric interaction between the methyl substituent and the tosyl group. The relative energies are shown in (Figure 9). The lowest energy transition state is *cis*-**TS-E**$_{ch}$, which most closely resembles a chairlike geometry, while *cis*-**TS-E**$_{bt}$ is only 0.2 kcal/mol higher in energy, and resembles a boatlike geometry.

Figure 7: Calculated aminocupration transition states for series E



The aminocupration transition states for the one ligand pathway F are shown in Figure 8. Again, the *cis*-product is favoured due to the lower transition state energies (lower by at least 3.1 kcal/mol) of *cis*-**TS-F**$_{ch}$ and *cis*-**TS-F**$_{bt}$ compared to *trans*-**TS-F**$_{ch}$ and *trans*-**TS-F**$_{bt}$. Their relative energies are shown in Figure 9. The lowest energy transition state is the *cis*-**TS-E**$_{bt}$, which is boatlike, and lower in energy than the chairlike *cis*-**TS-D**$_{ch}$ transition state by 0.2 kcal/mol.

The finding that both the boat and chair transition states leading to **4** are within 0.2 kcal/mol is not consequential to the diastereoselectivity of the reaction since both lead to the same product. However, if this trend is simi-

Figure 8: Calculated aminocupration transition states for series F.

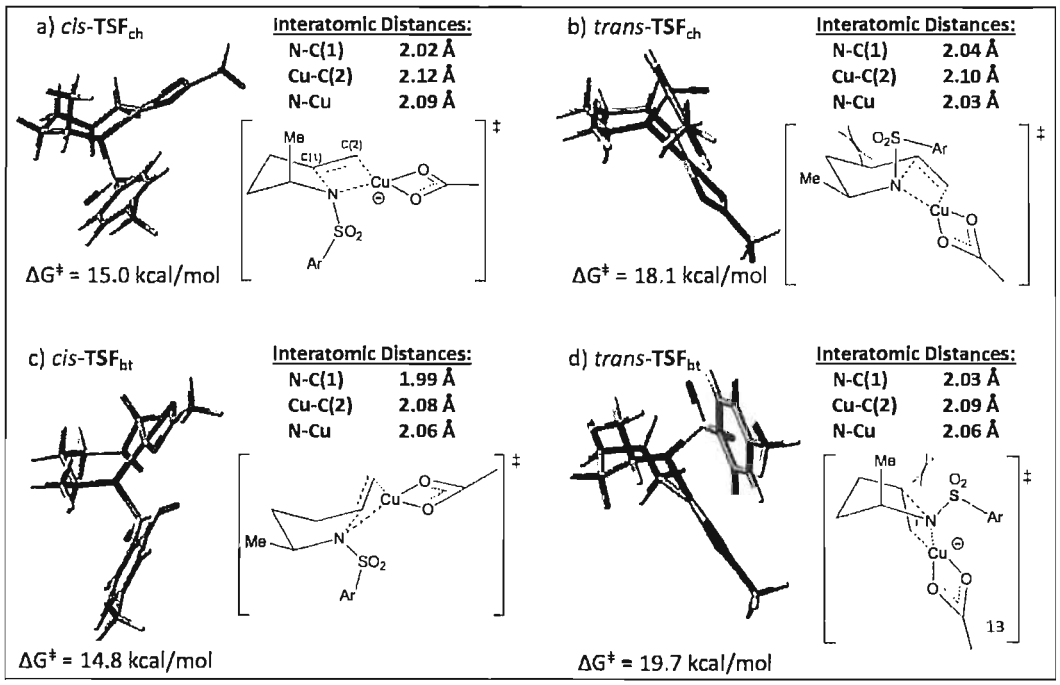
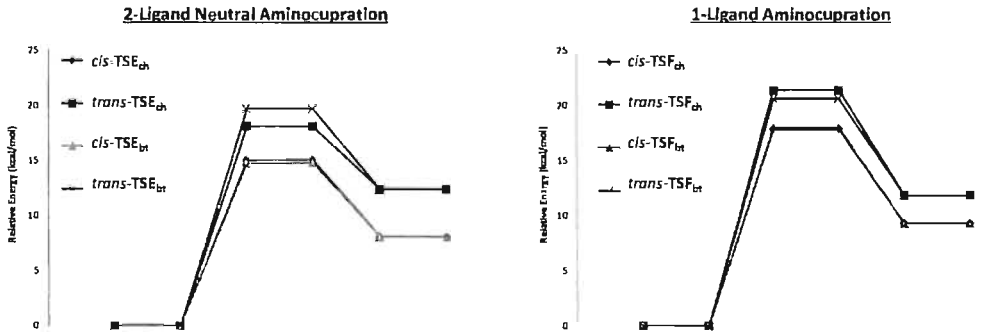


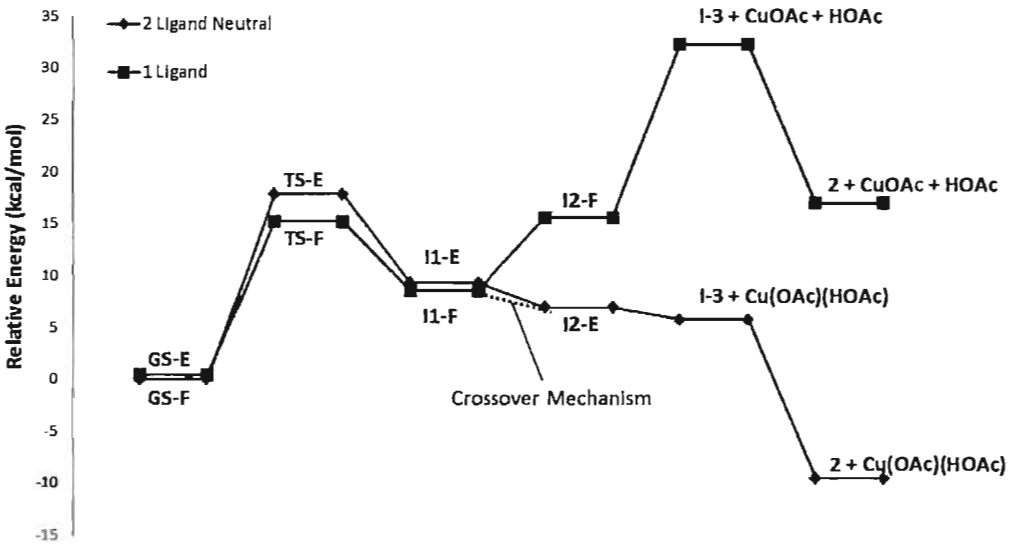
Figure 9: Calculated aminocupration transition state energies for series E and F.



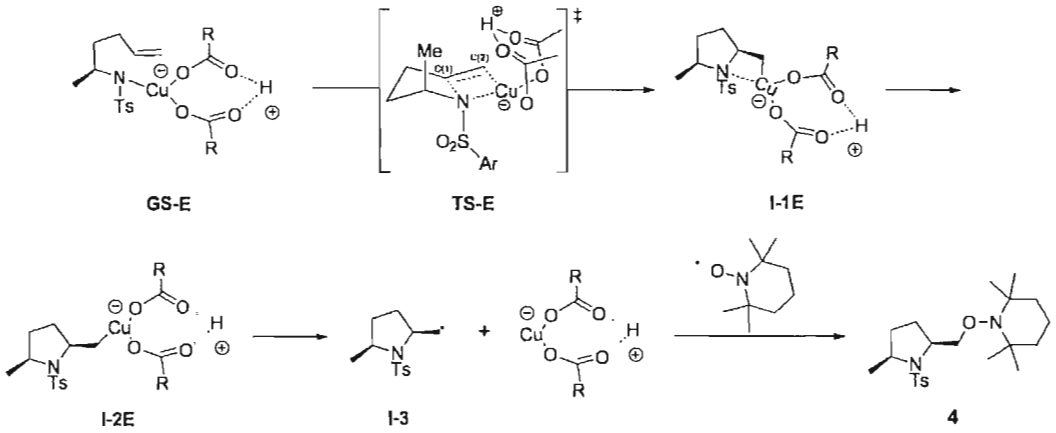
lar with Cu(II) catalysts coordinated by chiral bis-oxazoline ligands, it could translate to low levels of enantioselectivity in some reactions (e.g., substrates with α-substituents). In point of fact, this has actually been observed in a recently performed attempted desymmetrization reaction.[40] A comparison be-

tween the two mechanistic paths, E and F, is depicted in Figure 10, in which the lowest energy aminocupration transition states are supplemented by three additional minima on the energy landscape. The reprasentative scheme for pathway E is shown in Scheme 5.

Figure 10: Potential energy surface for the aminooxygenation of α-methyl-γ-alkenylsulfonamide, pathways E and F.



Scheme 5: 2 ligand neutral pathway E



The one-ligand mechanism (pathway F) is calculated to have a lower activation energy for aminocupration by 3.1 kcal/mol. The one-ligand mechanism, however, is disfavoured to undergo C-Cu homolysis due to the higher energy state of the Cu(I)OAc species. Again, a crossover mechanism may be active wherein aminocupration occurs with one ligand bound to copper, followed by coordination of a free HOAc ligand to facilitate homolysis. Taken together, it is important to note that despite having a higher activation energy for aminocupration, overall, the two-ligand, neutral mechanism (pathway E) is favored over the one-acetate-ligand mechanism (pathway F) due to the relative energetics of the C-Cu homolysis step. The two-acetate, neutral pathway E for the α-methyl-γ-alkenylsulfonamide **3** closely resembles the analogous pathway A for the *N*-tosyl-*o*-allylaniline **1**. The C-Cu homolysis in each of these reactions is exothermic by about 1 kcal/mol. The homolysis mechanism for the one-acetate neutral pathway F for the α-methyl-γ-alkenylsulfonamide **3** is also quite similar to the analogous pathway B for the *N*-tosyl-*o*-allylaniline. Breaking the N-Cu interaction in the initial aminocupration product to give the re-oriented intermediate, for example, **I-1F** to **I-2F** in the α-methyl series is endothermic by 7.0 kcal/mol. Likewise, in the aniline series, the conversion of **I-1B** to **I-2B** is endothermic by 9.0 kcal/mol. Similarly, C-Cu homolysis is endothermic in both series (**I-2E** to **I-E/F**, +16.7 kcal/mol; **I-2B** to **I-3**, +17.5 kcal/mol). The energy differences **I-1B** to **I-3** + [Cu(OAc)+HOAc)] and **I-1E** to **I-3E/F** + [Cu(OAc)+HOAc] are similar (26.5 and 23.7 kcal/mol); C-Cu homolysis through pathways B and F are energetically unfavorable and thus not reasonable mechanisms. In practice, the *N*-tosyl-*o*-allylaniline sub-

strate **1** is more reactive than the α-methyl-γ-alkenylsulfonamide **3** (**1** reacts at 110°C, while **3** requires heating to 130°C). This trend in reactivity is better reflected by the two-acetate neutral pathways (paths A and E, $\Delta G^{\ddagger}$ =17.2 and 17.9 kcal/mol, respectively) than the one-acetate pathways (paths B and F, $\Delta G^{\ddagger}$ =16.0 and 14.8 kcal/mol, respectively). Thus, it is possible that paths A and E more closely resemble the actual reaction mechanism, even in the aminocupration step. Additionally, since the diastereoselectivity is determined in the aminocupration step and the major diastereomer of the aminooxygenation, diamination and carboamination reactions are the same irrespective of base and ligands or conditions (catalytic versus stoichiometric copper catalyst), we can infer that the *cis*-aminocupration mechanism is relevant to all reactions in the class.

4.5 Conclusion (Section A)

The molecular modeling studies are largely consistent with the experimental results and also indicate a further role for the acetate ligands throughout the reaction coordinate. The calculated ground state structures and associated spin densities were instrumental to the EPR analysis and were able to predict that the entire class of reaction can be ran at lower temperatures. Furthermore, in our calculations we have found a strong ligand effect on the energies of ligand dissociation and C-Cu(II) homolysis. There are few theoretical studies of C-Cu(II) homolysis[50] and a ligand effect on bond dissociation energy has not previously been noted, although calculated ligand effects

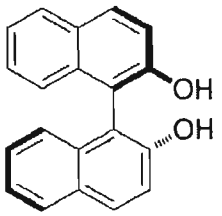
on single electron transfer involving copper complexes have been recently reported.[51] The results obtained from this work will greatly facilitate a subsequent detailed mechanistic analysis of the recently reported enantioselective Cu-catalyzed aminooxygenation of alkenes, which can open the door to a more detailed understanding of catalytic, enantioselective, Cu-catalyzed, alkene amination reactions. While the reaction kinetics are not expected to be identical, since the starting copper complexes in the enantioselective reaction are likely to be monomeric rather than dimeric, the stereochemical trends (diastereoselectivity) of the reactions are similar enough for us to anticipate similar kinetic isotope effects and rate-limiting step. The attractive qualities Cu(II) salts have to offer with respect to low expense, high versatility, and stereoselectivity ensure this reaction class will grow, thus a detailed mechanistic understanding as described herein should aid in the rational development of this class of reactions.

5 Section B - Hydrobenzoin Derivatives in Catalytic Asymmetric Reactions

5.1 Background/Introduction (Section B)

The discovery of new chiral ligands and auxiliaries continues to expand the frontiers of catalytic asymmetric synthesis. In particular, C_2-symmetric diols such as (S)-BINOL (**6**)[52] and (-)-TADDOL (**7**)[53] (Figure 11), have garnered considerable attention owing to the wide variety of asymmetric reactions which utilize these ligands and/or their derivatives. However, the list of C_2-symmetric diols is extensive and the success of one particular diol in a given asymmetric reaction does not necessarily correlate to success in other reactions. Oftentimes, catalytic asymmetric reactions employing a chiral ligand necessitate ligand screening to optimize yield and selectivity.

Figure 11: C_2-symmetric chiral diols



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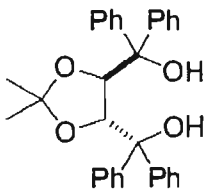

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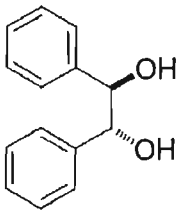


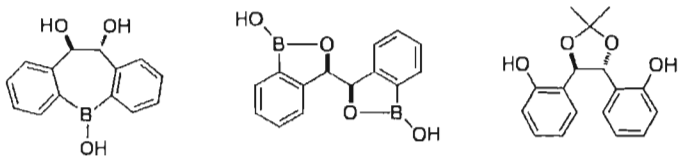
8

The advent of virtual ligand screening to accomplish such optimization is an important topic in computational chemistry, which if realized, would prove invaluable to the synthetic community. Conceptually speaking, one

could search vast online libraries of existing chiral ligands and select those which would provide the highest yield and selectivity for a reaction of interest. This type of concept has also been applied drug discovery, wherein a docking program attempts to identify small drug-like molecules which fit into a particular enzyme active site.[54] However, when working with proteins it is often necessary to use molecular mechanics methods, or very low level semi-empirical methods to describe such large systems, although more advanced methods such as fragment molecular orbital (FMO) theory[55] and ONIOM[56] are becoming more common. Unlike with large systems such as proteins and enzymes, catalytic reactions involving small molecules can be described using *ab initio* or high level semi-empirical methods such as DFT. This allows one to account for quantum effects such as secondary orbital overlap, orbital mixing, tunnelling, relativistic effects, hyperconjugation, and others, which often play instrumental roles in reaction mechanisms. As computational chemistry continues to improve it should become increasingly useful in the field of asymmetric catalysis, not just to gain further insight into the catalytic mechanism and catalyst properties, but as a tool for ligand and catalyst screening.

In 2009, a newly discovered direct functionalization of (*R*,*R*)-hydrobenzoin (**8**)[57,58] was reported. This methodology provided a unique opportunity to access untested chiral hydrobenzoin derivatives. This provided the perfect environment for an attempt to predict the activity of new ligands and/or catalysts with computational chemistry. With this in mind, three chiral derivatives were targeted for investigation (Figure 12).

Figure 12: Hydrobenzoin derivatives targeted for investigation



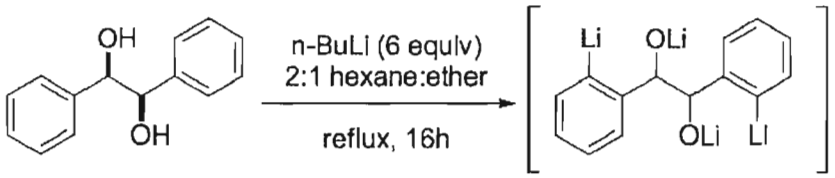
9 10 11

Borinic Acid **9** was one derivative of particular interest. The primary motivation for making **9** was that it may be the first chiral borinic acid catalyst. Properties such as the solubility and Brønsted acidity of **9** would be of additional interest, as they would greatly impact its utility as a catalyst. The second hydrobenzoin derivative of interest was bisbenzoxaborol **10**, for which a reliable synthesis was reported in the seminal publication.[57] **10** Was an intriguing candidate for investigation as few chiral boronic acids have ever been reported in the literature. As well, the presence of two boronic acid funcionalities within the same molecule stirred significant interest. The last derivative targetet for investigation, chiral diol **11**, has also previously been synthesized,[59] however despite a statement indicating that further investigation was underway to determine its utility as a chiral ligand, nothing was ever reported on its application. Using the newly developed direct funtionalization of hydrobenzoin, we could improve upon the previous synthesis and investigate this forgotten chiral ligand. In addition to investigating and predicting the utility of the aforementioned hydrobenzoin derivatives, we were intrigued by the interesting kinetics underlying the methodology for direct functionalization of hydrobenzoin and were keen on examining this process in greater detail.

5.2 *Ortho, ortho'* Functionalization of (*R*,*R*)-Hydrobenzoin.

The directed *ortho,ortho'*-dimetalation of (*R*,*R*)-hydrobenzoin (**8**) begins with deprotonation of the two alcohol groups by *n*-BuLi. The resulting lithium benzyl alkoxides serve as directed metalation groups (DMGs)[60–64] and facilitate formation of a bright orange/red tetralithio-intermediate, **12** (Scheme 6).

Scheme 6: Formation of tetralithio-intermediate **12**,

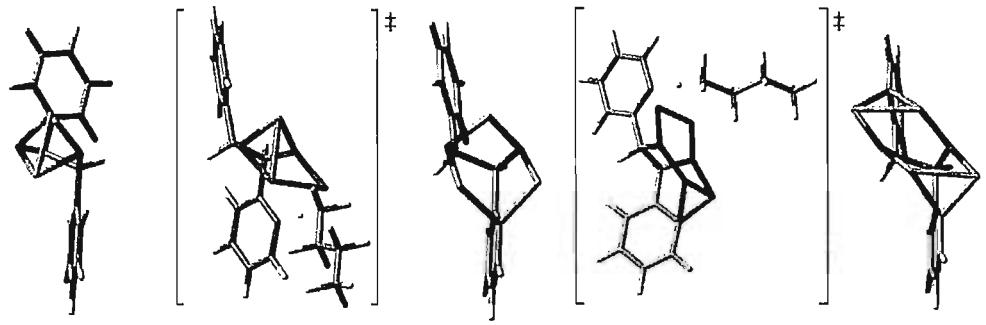


8 **12**

The formation of **12** was previously monitored by mass spectrometry following D_2O quench at 1 hour time intervals.[57] The resulting kinetics suggested that during the formation of **12** a relatively slow removal of the first *ortho* proton is followed by a more rapid removal of the second *ortho* proton. The hypothesis for the differing rates of DoM events observed during the D_2O quenching studies was that following the first *ortho*-metalation, the intermediate aryl lithium **14** may adopt a conformation in which the lithium alkoxide (DMG) and consequently the base (*i.e.*, *n*-BuLi or its aggregates) are positioned in close proximity to the *ortho* proton that is to be removed. It was thought that a model of these deprotonation events may support this hypothesis and provide insight into these aggregated intermediates.

The calculated intermediates and transition states for the formation of tetralithio-intermediate **12** are shown in Figure 13.

Figure 13: DFT B3LYP/6-31G(d) calculated intermediates and transition states for the formation of tetralithio-intermediate **12**.



All calculations were carried out using the Gaussian 09 and GaussView v5.08 programs. Geometry optimizations were performed at the Kohn Sham hybrid-DFT B3LYP level of theory using a 6-31G(d) basis set. The optimizations were performed at 338.15 K using the IEFPCM solvation method with the default parameters for diethyl ether. Subsequent single-point energy calculations were carried out using the second order Møller-Plesset perturbation theory (MP2) with a 6-31G(d) basis set. All optimized transition states were confirmed to be first-order saddle points by the appearance of a single imaginary frequency. Furthermore, the respective minima immediately preceding and succeeding the transition states were located using the Intrinsic Reaction Coordinate (IRC) method and confirmed to be minima by the appearance of only real vibrational modes. Transition states **TS-3** and **TS-4** are the transition states for the removal of the first and second ortho-protons respectfully. The use of a single molecule of base as opposed to an aggregated species, which is normally believed to exist in solution, was deemed acceptable for a number

of reasons. Firstly, precedence exists for the use of single molecules of alkyl-lithium bases in modeling deprotonations.[65] Secondly, the high temperatures (reflux) at which this reaction takes place are very dissimilar to the typical reaction conditions associated with alkyl-lithium deprotonations. As such, aggregation states normally observed among alkyl-lithium species are not likely at this temperature.

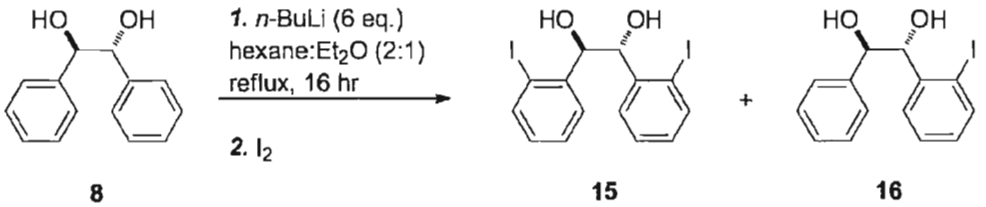
As anticipated, computations showed that the removal of the second *ortho* proton had a lower activation barrier than that of the first. The underlying cause was attributed to the differing structural alignments of the intermediates leading to the trilithio- and tetralithio-intermediates. It appeared, qualitatively, that the initial hypothesis was accurate, and the trilithiated intermediate was structurally oriented to facilitate the subsequent deprotonation. Undoubtedly dianion **13** is formed rapidly in the reaction mixture. The formation of trianion **14** proceeds through the deprotonation transition state **TS-3**, which has an activation energy of $E_a^{\ddagger} = 22.9$ kcal/mol. The corresponding metrics of this deprotonation event involve a bond-breaking C_{aryl}-H distance of 1.45 Å and a bond-forming C_{alkyl}-H distance of 1.50+ Å. The subsequent formation of **12** proceeds through transition state **TS-4**, with an activation energy of $E_a^{\ddagger} = 22.4$ kcal/mol. The key metrics of **TS-2** are a C_{aryl}-H distance of 1.45 Å and a C_{alkyl}-H distance of 1.48 Å. If one assumes that both deprotonation events have the same concentration dependency and pre-exponential factor, their relative rates can be approximated by the ratio of their rate constants according to the Arrhenius equation. This relationship indicates that the second deprotonation is about 2.2 times as fast as the first, consistent

with the reported kinetic data. The increased rate associated with deprotonation of the second ortho-position is a result of a system pre-organization. This pre-organization is apparent from the increased linearity of the phenyl rings in trilithio-intermediate **14** compared to dilithio-intermediate **13**. The increase in linearity can be quantified by the dihedral angle (θ) between the aromatic rings. For instance, the two aromatic rings in **13** are nearly orthogonal, $\theta = 62.0°$. An increase in planarity is observed at the transition state *TS-1* $\theta = 40.2°$. This corresponds to a difference of $\theta = 21.8°$ between **13** and **TS-1**. Furthermore, reorganization of **14** to **TS-2** requires a smaller change in the dihedral angle ($\theta = 9.6°$) between the two aromatic rings from $\theta = 33.9°$ in **14** to $\theta = 24.3°$ in **TS-2**. These results indicate that a larger structural change (in terms of torsion among the phenyl rings) is required to reach **TS-1** from dilithio-species **13** than to reach **TS-2** from trilithio-species **14**. It follows from these calculations that the aromatic lithium resulting from the first *ortho*-deprotonation coordinates to the O-Li group and increases the planarity of the aromatic rings. This structural change favorably aligns the molecule for the second *ortho*-deprotonation. It is noteworthy that comparable observations concerning the importance of structural organization of lithiated anions on reactivity have been previously reported.[66] Additionally, it is rather interesting to note that propagation along the reaction coordinate from the dilithio-intermediate **13** lends itself to the transient annihilation of C_2-symmetry in **14**, which is re-established upon formation of **12**. Of supplementary interest were the relative proton affinities of **12** and **14**. That of the trilithio-intermediate **14** was calculated to be 384.7 kcal/mol, while that of the

tetralithio-intermediate **12** was calculated to be 387.4 kcal/mol. These results are in line with the intuitive expectation that a tetralithiated species has a greater affinity for a proton than a trilithiated species. It is worth mentioning that proton affinity is a thermodynamic principle and thus is not related to the rate of deprotonation.

As an extension of this work, the directed *ortho,ortho'*-dimetalation of (*R,R*)-hydrobenzoin (**8**) was reinvestigated using I_2 as the electrophile quench (Scheme 7).

Scheme 7: Formation of **15**



8 **15** **16**

I_2 Was found to be the most responsive electrophile, next to D_2O, with a maximum of 53% conversion. Using I_2 as the electrophile, the reaction stoichiometry was investigated (Table 1). The use of sub-stoichiometric or stoichiometric (*i.e.*, 3.0, 3.5 and 4.0 equiv, Table 1 entry 1, 2 and 3) amounts of *n*-BuLi led to low isolated yields of the diiodohydrobenzoin **15**. Successively increasing the equivalents of *n*-BuLi provided a maximum isolated yield of **15**, of roughly 50% when 6 equivalents of *n*-BuLi were employed (Table 1 entry 9). During the evaluation of the reaction of the tetralithio intermediate **12** with I_2, we were surprised to find that monoiodohydrobenzoin **16** was produced in equivalent or lower yield than the diiodohydrobenzoin **15**, even at low overall conversion (*e.g.*, Table 1, entries 1, 2 and 3). One would expect,

Table 1: Optimization of the synthesis of diiodohydrobenzoin **15**

Entry	*n*-BuLi (eq.)	I_2 (eq.)	Ratio **15** : **16**[a]	Isolated Yield of **15** (%)
1	3	4	1.0 : 1.0	6
2	3.5	5	1.0 : 1.0	18
3	4	5	1.0 : 1.0	20
4[b]	4	5	1.0: 2.5	7
5	5	6	1.7 : 1.0	34
6[c]	5	6	1.0 : 2.6 [d]	8
7	6	7	5.0 : 1.0	51
8[e]	6	7	1.0 : 2.1[f]	13
9	8	9	5.0 : 1.0	53

[a] Ratio determined by analysis of ^{1}H NMR spectra recorded on crude reaction mixture. [b] TMEDA (4 eq.) was added prior to the addition of *n*-BuLi. [c] TMEDA (5 eq.) was added prior to the addition of *n*-BuLi.
[d] Hydrobenzoin (48%) was also recovered from this reaction.
[e] TMEDA (6 eq.) was added prior to the addition of *n*-BuLi.
[f] Hydrobenzoin (34%) was also recovered from this reaction.

as the reaction progressed, more of the trilithio-intermediate would be present than tetralithio-intermediate, as the former precedes the later. These results support the previous hypothesis that the rate-limiting step in the formation of the tetralithio-intermediate **12** may be the first D*o*M (*i.e.*, formation of a trilithio intermediate) and that the second DoM event is relatively more rapid. However, the D_2O studies clearly indicated that under the experimental conditions, the tetralithio-intermediate was produced in at least 92 % yield. Thus, the iodine studies seemingly indicate that the tetralithio-intermediate preferentially reacts twice with iodine rather than once.

Despite what appears to be a highly reactive molecule, tetralithio-intermediate **12** only gave the corresponding *ortho,ortho*'-difunctionalized product with ceratin electrophiles. The use many common electrophiles such as aldehydes, ke-

tones, amides, and benzyl halides all resulted in recovered starting material and/or an intractable mixtures of products. It was postulated that perhaps the addition of TMEDA would increase the reactivity of **12** towards electophiles. Accordingly, TMEDA was added to the reaction flask, prior to the addition of *n*-BuLi (Table 1, entries 4, 6 and 8). Presumably, TMEDA would assist in the disaggregation of organolithium species in the reaction. Unfortunately, no improvements were observed, and in fact resulted in lower overall conversions and isolated yields of diiodohydrobenzoin **15**. This result was perhaps to be expected if one considers that internal aggregation plays a role in facilitating both ortho-position deprotonations. It is likely that TMEDA served to disassemble the highly ordered transition geometry leading to the second ortho deprotonation, thus preventing formation of the tetralithiated species. Because the O-Li groups are the directing groups, even for the first ortho-deprotonation, it is likely that TMEDA prevents necessary aggregation at this stage as well. However, that TMEDA has a greater effect on the second *ortho* deprotonation than the first is apparent by the switch in product distrubution (Table 1). The increase in formation of **14** relative to **12** likely correlates to an increase in the rate of the first deprotonation relative to the second. Although it was not done, a kinetic analysis similar to that previously reported, but in the presence of TMEDA, would likely support this. With respect to the effect of TMEDA on the aggregation states of the base itself, TMEDA is typically used within reactions run at -78 °C, while the reaction in question is done under reflux. Therefore, it is not likely that *n*-BuLi exists as an aggregated species at this temperature and the reaction would not benefit from the addi-

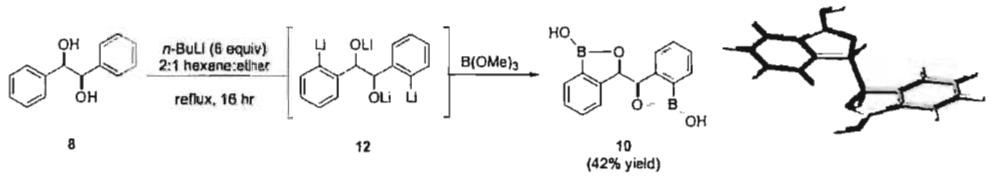
tion of TMEDA. What is more, TMEDA may simply act as a proton source for the tetralithio-intermediate (albeit a poor one). Though this is unlikely, it is supported by the poor yield of the diiodohydrobenzoin product (Table 1, entries 4, 6, and 8) for reactions run in the presence of TMEDA. It was clear that TMEDA interfered with the formation **12**. For this reason, we hypothesized that the addition of TMEDA would be more useful after the formation of **12**, added at a low temperature just before quenching with an electrophile. Since the deuterium quench study implied that the tetralithio-intermediate was indeed being completely formed, it was more likely that **12** was inherently unreactive to certain electophiles. It was postulated that TMEDA may act to dissociate any inter- and intra-molecular aggregation of **12**. As such, TMEDA was added at low temperatures before quenching with I_2 or benzaldehyde as electophiles. Freshly distilled TMEDA was added to **12** at -78 °C and allowed to stir for 20 minutes preceding the addition of electrophile. When benzaldehyde was used as the electrophile, only starting material was observed, while the use of I_2 provided a mixture of **16** : **8** : **15** in a ratio of 0.5 : 1 : 1.3. Despite the failue of this approach, it was interesting to find **15** was once again formed in higher concentration than **16**.

5.3 Bisbenzoxaborol Catalyst

Bisbenzoxaborol **10** was made by quenching tetralithio-species **12** with $B(OMe)_3$ at 0 °C (Scheme 8). The resulting yellow/white sludge is then warmed to room temperature and acidified to pH = 2, in order to hydrolyze

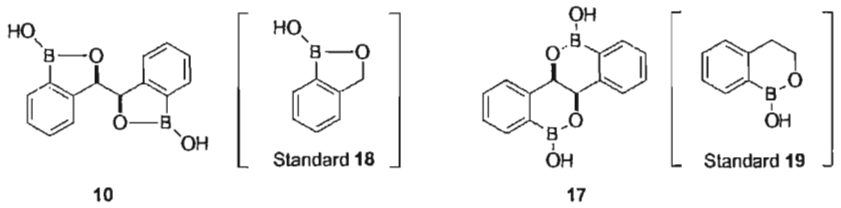
the methoxy groups. The reaction mixture is then neutralized and the product isolated by column chromatography in 42% yield.

Scheme 8: Synthesis of bisbenzoxaborol **10**.



The original structural assignment of **10** in terms of ring size (5-memberd isomer **10** vs 6-membered **17**, Figure 14) was based on the reported IR spectrum of a boronophthalide synthesized in 1959.[67] The spectrum had an infrared absorbtion band at 1000-900 cm^{-1} which was postulated to be the C-O band in the boronolactone ring. The presence of this same band in the IR spectra of **10**, resulted in its structural assignment. Nevertheless, the nature of this project necessitated a more assured structural assignment. Accordingly, 5-membered and 6-membered boronophthalides were used as standards, and their boron-NMR spectra were compared with what was beleived to be **10**.

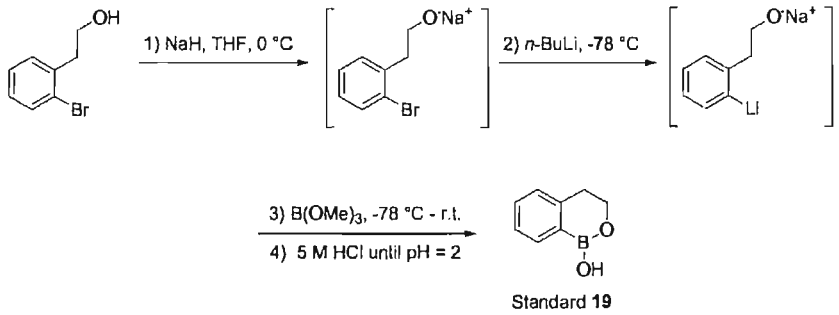
Figure 14: 5- and 6-membered bisbenzoxaborol isomers and their corresponding standards.



5-membered standard **18** was previously reported by Hall in 2006[68] while 6-membered standard **19** was synthesized as per Scheme 8. The B-NMR spectrum of **10** showed a peak at 28 ppm, while the spectra for **18** and **19** had

peaks at 27.5 ppm and 20 ppm respectively. This additional evidence supported the original structural assignment of **10**.

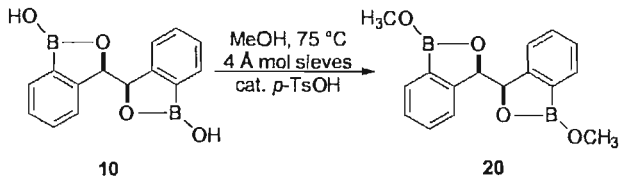
Scheme 9: Synthesis of standard **19**.



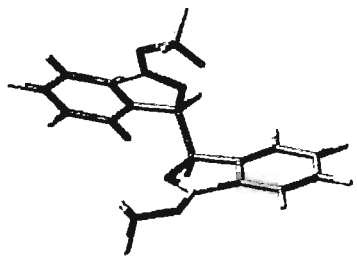
Standard **19**

We postulated that the two boronic ester functionalities of **20** would create a chiral Lewis acidic "pocket", capable of activating α-dicarbonyl compounds. Functionalizing **10** as the methyl ester **20** eliminated the Brønsted acid functionality, leaving only a Lewis acid. Synthesis of **20** was accomplished by refluxing **10** with methanol, a catalytic amount of *p*-TsOH, and 4 $\mathring{A}$ molecular sives (Scheme 10).

Scheme 10: Synthesis of Bisboronic ester **20**.



10 **20**



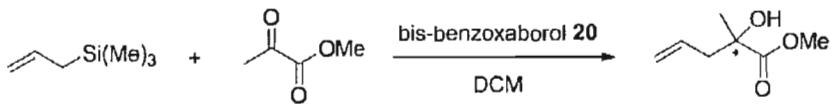
To probe the catalytic ability of **20**, a model was constructed to examine its interaction with the α-dicarbonyl, methyl pyruvate. Despite scanning various combinations of basis sets and functionals, no unconstrained minima could

be located in which the two carbonyl oxygens were bound/coordinated to the two boron atoms. This suggested that the structural realignment required for **20** to accomodate α-dicarbonyl compounds was unfavourable, despite the added electronic stability of oxygen lone pair induction into the empty p-orbitals. Consequently, it was then postulated that the ketone oxygen of methylpyruvate may fit by itslef into the Lewic acid pocket of **20**, and become dualy activated by both boron atoms. Again, no unconstrained minima could be located for this structure, and no interaction was present between the ketone oxygen and either of the two boron atoms. As such, the computational results suggested that **20** was not sufficiently Lewis acidic for the proposed chemistry. Thus, it was alternatively envisioned that **10** may act as a chiral based Brønsted acid catalyst. Analogous to the intended application of **20**, it was thought that the two boronic acid functionalities would coordinate the two carbonyl oxygens of an α-dicarbonyl compound. Supporting this concept was the calculated ground state minima between methylpyruvate and **10**, which showed stabilizing hydrogen bond contacts (2.0 $\AA$ to the ester oxygen and 1.97 $\AA$ to the ketone oxygen). Unfortunately, there was no energetic preference between having the re- or the si-face of the ketone exposed, indicating that the chiral backbone of the catalyst was too far removed from the site of coordination to induce any appreciable levels of selectivity. Although these preliminary computational results were rather disappointing, and did not lend themselves to the proposed application of **20** or **10**, experimental testing was required to confirm or refute the theoretical data.

5.3.1 Hosomi-Sakurai Reaction

The Hosomi-Sakurai reaction[69] is a Lewis acid mediated allylation of aldehydes and ketones, using allylsilanes. The resulting homoalyllic alcohols often contain a new sterogenic center, and thus the Hosomi-Sakurai reaction provided an excellent framework to investigate the ability of **20** as a chiral Lewis acid. Accordingly, allyltrimethylsilane was reacted with methyl pyruvate in the presence of a catalytic amount of **20** (Scheme 11).

Scheme 11: Hosomi-Sakurai Reaction



Unfortunately, even with the addition of 50 mol% of **20**, and heating to 50 °C (Table 2, entry 4) no reaction was observed by TLC or ^{1}H-NMR. Considering the computational results, this lack of reactivity was not surprising. It was thus concluded that **20** was either not acting as a Lewis acid, or it was not sufficiently Lewis acidic to catalyze this particular reaction.

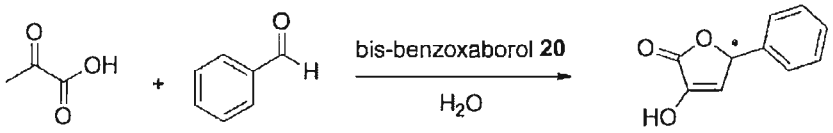
Table 2: Experimental Results for the Hosomi-Sakurai Reaction catalyzed by bisboronicester **20**.

Entry	mol % of catalyst **20**	Temperature (°C)	% Conversion
1	5 %	25 °C	0 %
2	5 %	50 °C	0 %
3	10 %	50 °C	0 %
4	50 %	50 °C	0 %

5.3.2 Aldol Reaction

To further investigate the ability of **20** to activate α-dicarbonyl compounds through Lewis acid coordination, the direct aldol reaction of pyruvic acid with benzaldehyde (Scheme 12) was performed in the presence of **20**.

Scheme 12: Boron-Catalyzed Direct Aldol Reaction of Pyruvic Acid.



A recent report[70] revealed that aryl boronic acids are able to catalyze the direct aldol reaction between pyruvic acids and benzaldehyde, using water as solvent. Moreover presedence exists for using 'soft' Lewis acids to promote the reaction.[71,72] It was envisioned that **20** could improve upon this reaction by introducing a chiral environment, thereby affording enantioenriched products. By coordinating pyruvic acid, **20** might stabilize its enol tautomer, thus driving the reaction forward. After various attempts (Table 3), no product was observed by TLC or ^{1}H-NMR and it was thus concluded that **20** was not able to catalyze the direct aldol reaction of pyruvic acid with benzaldehyde. At this state it was likely that the computational results were accurate, and **20** would not be able to activate α-ketoesters through Lewis acid coordination. Thus, employing **20** as a Lewis-acid catalyst was abandoned and investigation continued into the utility of **10** as a chiral Brønsted acid catalyst. As such, the direct aldol reaction was repeated using bisboronic acid **10**. Once again, no product was observed by TLC or ^{1}H-NMR for any of the experimental conditions tested (Table 3).

Table 3: Experimental results for the Direct Aldol Reaction

Entry	mol % of catalyst **10** or **20**	Solvent	% Conversion
1	10% of **20**	H2O	0%
2	10% of **10**	H2O	0%
3	30% of **20**	H2O	0%
4	30% of **10**	H2O	0%
5	10% of **20**	DCM	0%
6	10% of **10**	DCM	0%
7	10% of **20**	MeOH	0%
8	10% of **10**	MeOH	0%

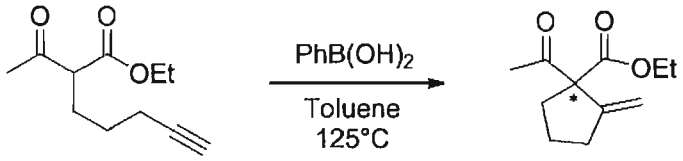
This was a particularly dissapointing result, as it had been reported that catalytic quantities of phenylboronic acid provided the product in 19% yield. Often when a boronic acid catalyzed reaction is attempted, phenylboronic acid is the first catalyst to be screened due to its availability and low cost, and further modification is necessary to obtain useful yields and/or selectivity. The fact that **10** so closely resembles phenylboronic acid yet did not succeed in catalyzing the reaction to any extent, indicated that it may not be active enough to catalyze reactions of interest involving α-dicarbonyl compounds.

5.3.3 Conia ene Reaction

Recently the group of Dixon[73] published a boronic acid catalyzed Conia ene reaction of acetylenic dicarbonyl compounds (Scheme 13). Given the negative results obtained with α-dicarbonyl compounds, a change in substrate to β-dicarbonyl compounds seemed appropreate within the investigation of **10** as an asymmetric catalyst.

A ground state calculation indicated that the β-dicarbonyl, acetoacetate,

Scheme 13: Conia ene Reaction

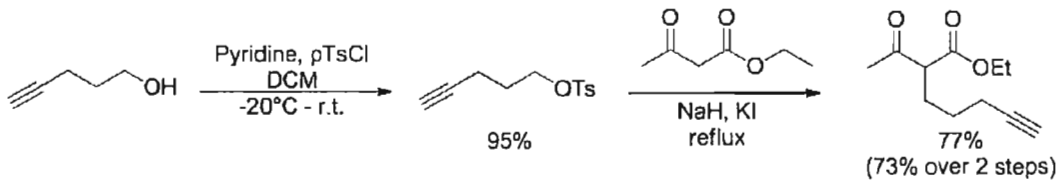


coordinated to **10** in much the same way as α-dicarbonyl compounds. A significant difference however, was that the β-dicarbonyl did not have to twist so unfavourably about the central C-C bond to be properly aligned. Accordingly, transition state calculations were performed to determine if Brønsted acid coordination by **10** was sufficient to catalyze the Conia ene reaction. Initially, the uncatalyzed pro-(R) and pro-(S) transition states were modelled, and were calculated to have activation barriers 32.3 and 32.4 kcal/mol respectively. This was expected, as there is no structural bias between the two enantiomeric transition states. In the Brønsted acid catalyzed reaction, two coordination modes were possible, albeit very similar ones. Each coordination mode was accompanied by a pro-(R) and a pro-(S) transition state, leading to four possible transition state structures in the Brønsted acid catalyzed mechanism. The Brønsted acid catalyzed pro-S transition states for the two coordination modes were calculated to have activation barriers of 30.0 kcal/mol and 28.5 kcal/mol. The coordination mode favoured by activation energy also had a lower transition state energy by 1.1 kcal/mol. Thus, the accompanying pro-R transition state was modelled for the favoured coordination mode. The two enantiomeric transition sates led to identical activation barriers to one decimal place. Despite the predicted lack of selectivity imparted by **10**, the computations did indicate the activation barrier was reduced by 3.9 kcal/mol.

Accordingly, the reaction was carried out in order to determine if **10** could succesfully catalyze the reaction, and if so, with what selectivity.

The starting material was prepared from pentyne-1-ol (Scheme 14). First, the alcohol was reacted with *p*-toluenesulfonyl chloride to provide the necessary leaving group. Mesylate and chloro leaving groups were also attempted, but provided poor yields in the addition step. Addition of the resulting tosyl alkyne to ethyl acetoacetate was acheived using NaH and a catalytic amount of KI.

Scheme 14: Synthesis of Starting Material for the Conia Ene Reaction



The reaction was first run inside an ^{1}H-NMR tube at 110 °C in C_6D_6, in order to moniter the progress by ^{1}H-NMR. The appearance of product was apparent within the first hour, accompanied by an equivalent decrease in substrate signal (see SI for spectra). No side products were observed. Further optimization of the reaction conditions indicated that in the presence of **10**, the reaction could be run at temperatures as low as 60 °C (Table 4).

As expected, the protic solvent ^{i}PrOH and the coordinating solvent THF, completely inhibited the reaction. Additionally, polar, aprotic solvents were the most effective, and aromatic solvents led to increased yields. This can be attributed to solvent stabilization of the highly polarized transition state and favourable pi-pi stacking between the solvent and the catalyst. The resulting

Table 4: Experimental Results for the Conia ene Reaction

Entry	Solvent	Temperature	Approximate Yield (%) After 24 h	% *ee*
1	C_6D_6	125 °C	50 %	0
2	toluene	125 °C	50 %	ND
3	toluene	100 °C	50 %	0
4	toluene	60 °C	25 %	0
5	^{i}PrOH	100 °C	trace	ND
6	THF	100 °C	trace	ND
7	1,2-dichloroethane	100 °C	65 %	0
8	1,2-dichlorobenzene	100 °C	75 %	0
9	1,2-dichlorobenzene	50 °C	40 %	0

* All reactions were performed using 5 mol% of **10**.

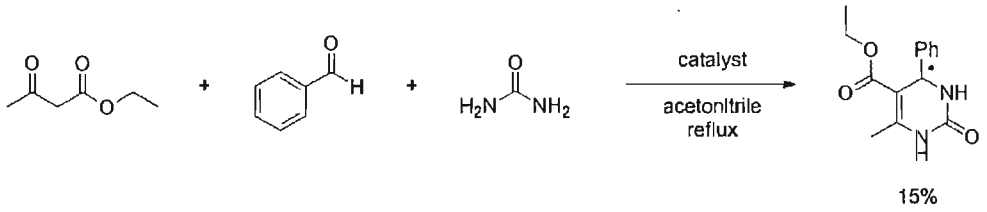
products were purified by column chromatography, and the uncalibrated GC-MS was utilized to determine the enantioselectivity. The GC-MS run used a Chirodex-3 column with an 80 °C isotherm. The purified produc s of selected reactions were run consecutively, at 10 minute intervals, each product sample requiring approximately 3.5 hours for elution. Unfortunately, all of the reactions provided racemic products, confirming the lack of selectivity predicted by the computational models. Nevertheless, **10** was successful in catalyzing the Conia ene reaction, which was also consistent with the computational results. Moreover, the computed transition state structures suggest that proper functionalization of the catalyst may provide increased selectivity, and may warrent further investigation beyond the scope of this research project.

5.3.4 Biginelli Reaction

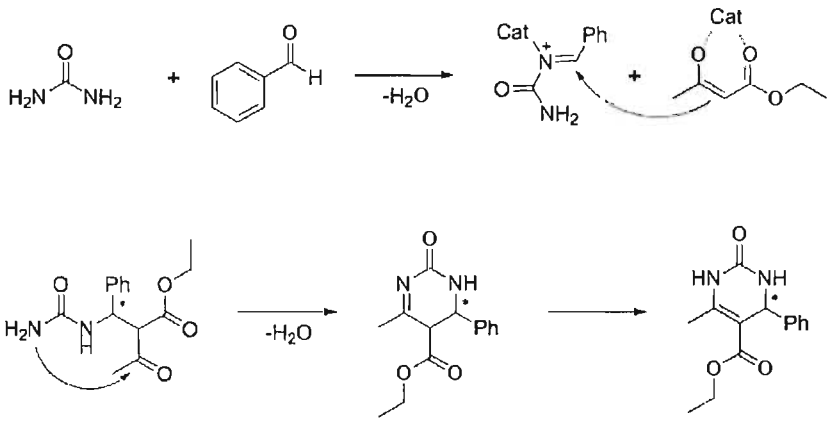
The successfully catalyzed Conia ene reaction indicated that while **10** may not suficiently activate α-dicarbonyl compounds, it can activate β-dicarbonyl compounds. However, the utility of **10** was clearly limited by the lack of selectivity imparted to the reaction. In this vein, it was postulated that **10** might provide reasonable levels of selectivity in the Biginelli reaction (Scheme 15), due to the nature of its mechanism (Scheme 16). First discovered in 1893,[74] the Biginelli reaction is a one-pot, three-component condensation reaction between an aromatic aldehyde, urea, and ethyl acetoacetate and can be catalyzed by a variety of Lewis and Brønsted acids. Attention was drawn to this reaction by a recent report in which phenylboronic acid was successful in catalyzing the Biginelli reaction.[75] Of particular interest was the supposed reaction mechanism, in which two equivalents of catalyst were envoked in the stereochemistry determining step in which the enol form of acetoacetate attacks the intermediate N-acyliminium ion to form the open chain ureide. The computational work in the Conia ene reaction suggested that **10** failed to provide selectivity because its chiral backbone was too far removed from the C-C bond formation. However, because the proposed mechanism involves two equivalents of catalyst during the stereochemistry-determining step (one on each reacting component), they might interact above the site of C-C bond formation, and in turn induce selectvitity.

Because of the uncertainty of the reaction mechanism, and the complexity involved in designing a mechanistic model in relation to running the

Scheme 15: General scheme for the Biginelli reaction.



Scheme 16: Proposed mechanism of the Biginelli Reaction.

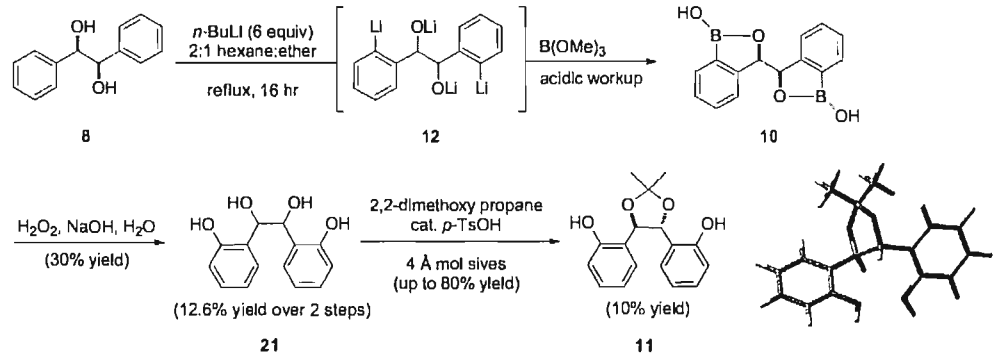


experiment, the reaction was attempted prior to any computational modeling. Moreover, the aforementioned computational and experimental results had proven that **10** was able to activate β-dicarbonyl compounds. Gratifyingly, **10** was successful in catalyzing the Biginelli reaction, although in low yield (15% isolated yield after recrystalization). Much to our dissapointment, however, optical rotory analysis indicated that the product was racemic. It was thus concluded that while **10** is capable of activating β-dicarbonyl compounds, in its present form it is not a fruitful chiral catalyst.

5.4 Chiral diol ligand

We next turned to the C_2-symmetric diol **11**, and its possible use as a chiral ligand in asymmetric catalysis. The only previously reported synthesis of chiral diol **11** was in 1996 by Kanemasa et. al.[59] The synthesis was reasonable in terms of starting material (salicylaldehyde), yield, and step economy (11% yield over six steps) but suffered greatly from a practical standpoint. Over the six step synthesis, two crystalizations and four column chromatography steps were required for the isolation of intermediates and the final product. Although the synthesis reported herein produced **11** in a lower overall yield (10%), it presents a substantial improvement in terms of practicality (Scheme 17).

Scheme 17: Synthesis of chiral diol **11**.

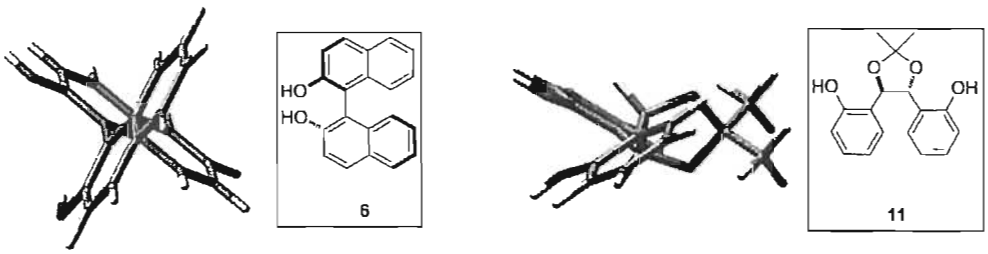


The synthesis of **11** began with the *ortho,ortho*'-dimetalation of **8** followed by the addition of trimethoxyborate to provide bis-benzoxaborol **10**. Without further isolation or purification, a subsequent hydrogen peroxide oxidation afforded the tetrol **21** in 13% overall yield after isolation by chromatography. **21** Was then converted to the diphenyl acetonide **11** using a catalytic amount of *p*-TsOH and 2,2-dimethoxypropane as solvent (10% overall yield

after isolation by chromatography). The synthesis provided the target compound in three steps, with similar yield to the previously reported synthesis, only two column chromatography steps, and no crystalization required.

An optimized structure of **11** at the B3LYP/6-31G(d) level of theory provided insight into its structural geometry. The geometry resembled that of (*R*)-BINOL(Figure 15), however its natural bite angle was calculated to be only 60.4° as opposed to the natural bite angle of BINOL which was calculated to be 86.8°. A larger bite angle is normally beneficial, as it provides a larger chiral surface area. Nevertheless, the ability of **11** to chelate a metal center and provide a suitable chiral environment was investigated in the titanium catalyzed asymmetric addition to diethyl zinc.

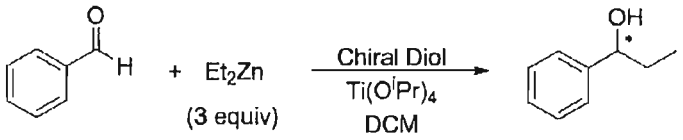
Figure 15: DFT calculated minima of (*R*)-BINOL and chiral diol **11**.



5.4.1 diethyl zinc addition

The addition of diethyl zinc (Scheme 18) to benzaldehyde has become the standard for screening new C_2-symmetric chiral diols as asymmetric ligands.

Scheme 18: Addition of diethylzinc to benzaldehyde



As well as being an ideal testing ground, the addition of diehtyl zinc also presents significant mechanistic interest due to the uncertainty surrounding the active catalytic species and the interesting effects observed when using and omitting a titanium co-catalyst. Substantial research has focused on the mechanism of the Ti(O-iPr)$_4$ mediated diethyl zinc addition.[76,77] It has been observed that both the yield and selectivity of diethylzinc additions are strongly affected by the presence of Ti(O-iPr)$_4$. Reactions carried out in the presence of Ti(O-iPr)$_4$, are often accompanied by an increase in yield and a reversal of product stereochemistry compared to reactions carried out in the absence of Ti(O-iPr)$_4$. The reversal of product stereochemistry is atrributed to a change in mechanism. In the absence of Ti(O-iPr)$_4$, the alkyl group is transfered directly from the Zn atom. Alternatively, in the presence of Ti(O-iPr)$_4$, the alkyl group is transfered from Zn to Ti, and subsequently to the aldehyde. In the Zn-mediated mechanism, the ligand backbone dictates the stereochemistry. However, in the Ti-mediated mechanism the ligand backbone causes the bound Ti(O-iPr)$_4$ complexes to change their geometry. This change in geometry about the ligands on Ti, subsequently produce a new chiral environment for the addition, and the presence of an intermediate chiral environment forces a reversal of the stereochemical preference of addition. Currently, a (BINOLate)Ti(aldehyde) (O-iPr)$_2$Ti(O-iPr)$_3$Et intermediate is beleived to

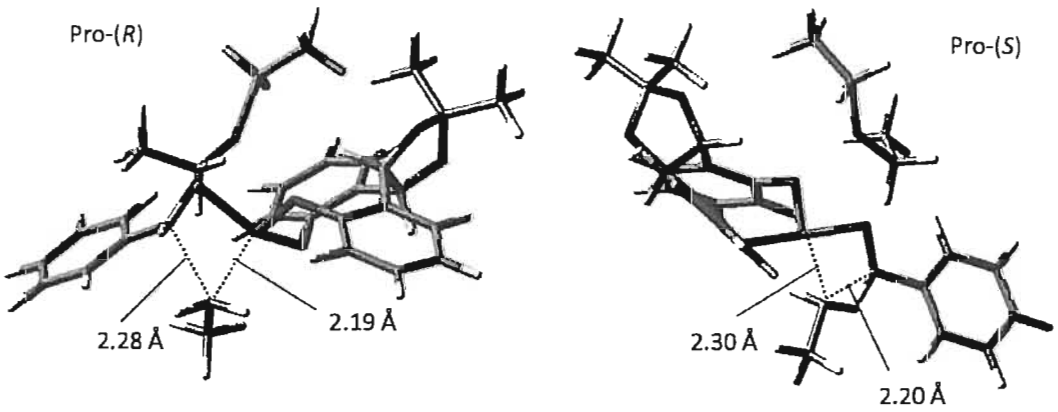
be the active species in reactions using Ti(O-iPr)$_4$ and is well supported by experimental evidence.[76] To date, the only proposed transition state for the titanium-free addition of diethylzinc to benzaldehyde with a chiral diol ligand was presented in 2008.[77] However, the proposed mechanism is speculative, and the authors are quick to note: "A reaction mechanism detailing the key difference between the zinc-mediated and titanium-mediated pathways remains to be developed."

In light of this mechanistic curiosity, transition state assemblies for the addition of diethylzinc to benzaldehyde employing chiral diol **11** were computed in the presence and absence of Ti(O-iPr)$_4$, as proposed by Walsh and Hithcock respectively.[76,77] Calculations were run at the B3LYP/6-31G(d) level of theory. The control reaction, without chiral diol **11** was not modelled. The computational results shared similar characteristics with existing experimental results on diethylzinc additions using BINOL. The computed Ti-mediated addition of diethyl zinc favoured the (*R*)-enantiomer, with an activation barrier of 17 kcal/mol. In contrast, the calculated Zn-mediated addition showed no preference for either enantiomer ($\Delta G^{\ddagger} = 0.0$ kcal/mol) and had a larger activation barrier of 24 kcal/mol. Taken together, the computations show increased yield and selectivity for the Ti(O-iPr)$_4$ mediated addition, consistent with existing experimental results. Unfortunately, however, due the absence of any calculated selectivity for the Zn-mediated mechanism, no information was aquired regarding the reversal in product stereochemistry.

The pro-(*R*) and pro-(*S*) transition state structures for the addition in

the absence of Ti(O-iPr)$_4$ are shown in Figure 16. Both transition states share similar features. In each transition state the benzaldehyde is simultaneously activated by both Zn atoms, and the ethyl group is being transfered from the Zn atom bound to both oxygens of the ligand. The second Zn atom still exists as Et_2Zn and is coordinated to one of the oxygen atoms of the ligand. The C-C bond forming distances are 2.28 $\AA$ for the pro-(R) TS and 2.30 $\AA$ for the pro-(S) TS, only slightly longer than the Zn-C bond breaking distances of 2.19 $\AA$ and 2.20 $\AA$.

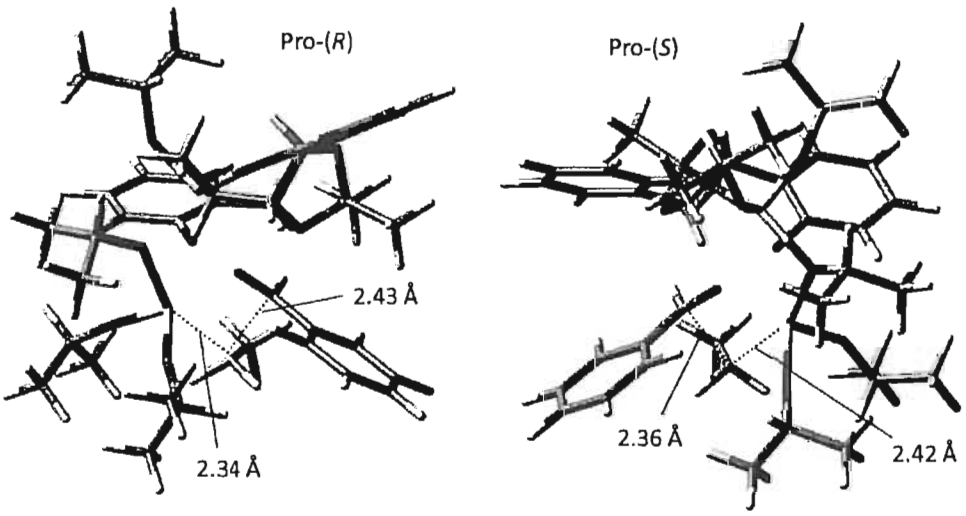
Figure 16: Calculated pro-(S) and pro-(R) transition states for the addition of diethylzinc to benzaldehyde in the absence of Ti(O-iPr)$_4$.



The pro-(R) and pro-(S) transition state structures for the addition in the presence of Ti(O^{i}Pr)$_4$ are shown in Figure 17. Analogous to the Zn mediated addition, the aldehyde is doubly coordinated by both Ti atoms. Moreover, the Ti(aldehyde)(O-iPr)$_2$ species is bound to both alcohol groups of the ligand and the Ti atom of the Ti(O-iPr)$_3$Et species is coordinated to one oxygen atom of the ligand. The Ti(O-iPr)$_3$Et species is further stabilized by an O-iPr ligand bridging between the two Ti atoms (O-Ti bond lengths of 2.00 and 2.11

Å for the pro-(R) TS and 2.06 and 2.02 Å for the pro-(S) TS). One significant difference from the Zn-mediated addition is that the ethyl group is not transfered from the Ti atom bound to the ligand, but instead from the Ti which is only coordinated to one of the ligand's oxygen atoms. It is likely that this switch in location of alkyl transfer is a primary factor in the observed reversal of stereoselectivity in the BINOL mediated additions. Lastly, the C-C bond forming distances are 2.43 Å for the pro-(R) TS and 2.43 Å for the pro-(S) TS, which are again slightly longer than the Ti-C bond breaking distances of 2.34 Å and 2.36 Å.

Figure 17: Calculated pro-(S) and pro-(R) transition states for the addition of diethylzinc to benzaldehyde in the presence of Ti(O-iPr)$_4$.



The experimental results using **11** were in good agreement with the calculations and proved to be consistent with many aspects of the existing experimental results employing (R)-BINOL (Table 5). In the absence of Ti(O-iPr)$_4$, the addition proceeded slowly, providing modest yield and no selectivity. Ex-

Table 5: Experimental results for the addition of diethylzinc to benzaldehyde.

Entry	Ti(O-iPr)$_4$	Temperature	Yield With Ligand **11**	Yield Without Ligand **11**	% ee^a
1	1.5 eq.	-20 °C	10 %	0 %	ND[b]
2	1.5 eq.	4 °C	40 %	25 %	13 %
3	1.5 eq.	23 °C	85 %	70 %	11 %
4	0 eq.	-20 °C	0 %	0 %	N/A[c]
5	0 eq.	4 °C	19 %	18 %	0 %
6	0 eq.	23 °C	50 %	50 %	0 %

* All reactions were run for 16 hours and performed using 5 mol% of **11**.
[a] Enantiomeric excess determined by a non-calibrated chiral HPLC.
[b] Not determined (insufficient product to obtain an HPLC trace).
[c] Not applicable.

actly the same results were observed in the control reaction, carried out in the absence of **11**. Although these results did not bode well for the application of **11** as a chiral ligand, they did serve to validate the computations, which predicted a slow rate of reaction and no selectivity. In contrast, in the presence of Ti(O-iPr)$_4$, the addition proceeced relatively more quickly, both with and without **11**. This time, however, the reactions employing **11** proceeded slightly faster and with slightly higher yields than the control reactions carried out in the absence of **11**. Accordingly, the Ti-mediated additions carried out in the presence of **11** provided improved yields and low selectivity for the (*R*)-enantiomer.

It is important to note that in the presence of a Ti co-catalyst, using ligand **11** derived from (*R*,*R*)-hydrobenzoin (**8**), the same enantiomer was favoured as the reported reactions using (*R*)-BINOL (**6**). As such, it is likely that the mechanism of the reaction employing **11** is equivalent to those which

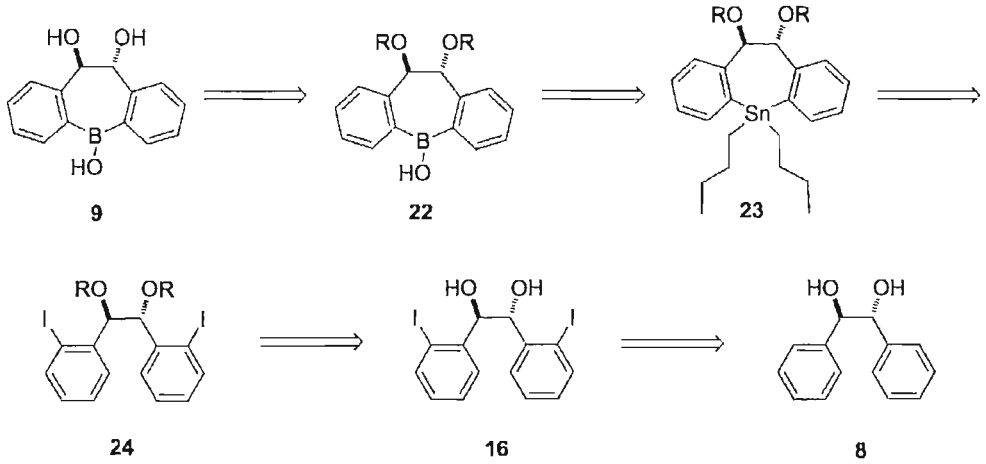
employ (*R*)- or (*S*)-BINOL (**6**). Furthermore, the consistency of the computations with the accompanying experimental results, and the reasonable activation barriers calculated for the reaction, supports the currently accepted mechanism as well as the proposed catalytic species for the diethyl zinc addition in the presence and absence of $Ti(O\text{-}iPr)_4$. Given the parallels between the reaction sets employing **8** and **6**, it is likely that the difference in selectivity is related to the difference in bite angle, with a large bite angle providing better *ee*'s. This conclusion is important to future research in this area, and may provide an important basis for selecting ligands for similar reactions.

5.5 Borinic Acid Catalyst

Perhaps the most interesting target in terms of both theory and application was chiral borinic acid **9**. In fact, bisbenzoxaborol **10** was only discovered by accident while attempting to synthesize **9**. The intent was to make the first chiral borinic acid catalyst, and to study its catalytic properties theoretically and experimentally. As such, a new synthetic approach was envisioned (Scheme 19), relying on the *ortho,ortho'* functionalization of (*R,R*)-hydrobenzoin, and a tin-boron exchange.

The synthesis began with the formation of diiodohydrobenzoin **16**. Protecting the alcohol functionalities as methoxy groups allowed a lithium halogen exchange to provide an *ortho,ortho'*-dilithiated intermediate, **25a**. Quenching with Cl_2SnBu_2 provided the organostannane **23a** in a maximum of 21% yield. At that stage, the computed structural geometry of these hydroben-

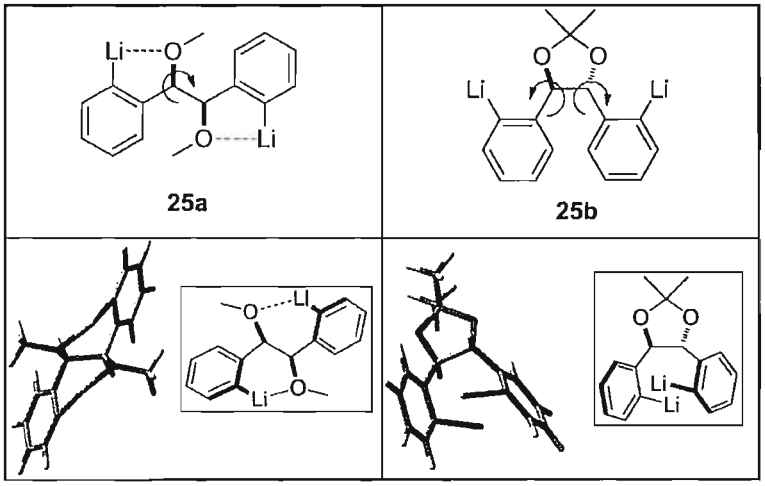
Scheme 19: Retrosynthetic analysis for **9**



zoin derivatives provided valuable insight into the origins of the low product yield. Coordination of the *ortho*-aryllithium atoms to the adjacent methoxy group oxygens restricted rotation around the Aryl-C-C-O dihedral, while allowing rotation around the O-C-C-O dihedral (Figure 18). This aligns the Li atoms on opposite ends, hindering the reactivity with Cl_2SnBu_2. Calculations confirmed this hypothesis, indicating that the molecule is 1.9 kcal/mol more stable when the Li atoms are coordinated to oxygen atoms than when they are positioned opposite to the OMe groups.

It was hypothesized that an acetonide protecting group may restrict rotation around the central O-C-C-O bond and prevent coordination of the Li atoms to the oxygen atoms. Additionally, this would effectively place the *o*-lithium atoms in a favourable position to react with Cl_2SnBu_2 and form organostannane **23b**. A subsequent set of DFT calculations supported this hypothesis, indicating that the lowest energy structure positioned the two Li atoms adjascent to one another, opposite the acetonide ligand (Figure 18). The

Figure 18: Ground state geometries of the intermediates **25a** and **25b**.



next lowest energy structure was calculated to be 2.8 kcal/mol less stable and had one Li atom positioned opposite the acetonide and the other coordinated to one of the acetonide oxygens. In accordance with the computational insight, when acetonide **25b** was reacted with Cl_2SnBu_2, the resulting organostanane **23b** was produced in 50%, an increase in yield of 30%. This set the stage for a tin-boron exchange. A recent report on the synthesis of B-antecenes[78] provided an ideal synthetic protocol for the transformation. However, much to our dissapointment, upon subjecting organostannane **23b** and **23a** to the conditions reported by Tovar and Caruso, pure starting material was recovered, signifying that the tin-boron exchange did not take place. Even after allowing the reaction to proceed for 24 hours, followed by warming to room temperature, only starting material was recovered. At that stage attempts were made to execute the exchange using different boron sources. $BOMe_3$, BCl_3 and BH_3 were attempted to no avail. Organostannane **23b** was reacted with BH_3 in toluene at 100 °C for four days, and clean starting material was re-

covered. A final attempt was made using BCl_3 in heptane at 100 °C followed by a methanol quench. Promisingly, three new spots were observed on the TLC plate. Due to the small scale of the reaction, a preperative TLC was preformed in order to isolate these fractions. Of these three fractions, two of them showed promising features by ^{1}H-NMR (See SI). These features included the dissapearance of Sn (apparent from the loss of satelites about the methylene singlet), a symmetrical geometry (apparent from the aromatic protons and the singlet methylene signal), and an upfield shift in the methylene signal relative to bisboronic acid **11**. In an attempt to characterize these fractions, they were reacted with ethanolamine overnight in toluene at 50 °C. Unfortunately, the resulting ^{1}H-NMR spectra were difficult to interpret, and the characterization was not possible. Therefore, without the ability to synthesize **9**, its chemistry was not studied further.

5.6 Conclusion (Section B)

Although the particular hydrobenzoin derivatives studied during this project did not produce sufficient selectivity as catalysts or ligands in the asymmetric reactions investigated, they represent only a small fraction of the possible hydrobenzoin derivatives. More importantly, the investigation proved valuable for validation of theoretical data and demonstrated the ability of computational chemistry to predict synthetic organic reactions. The bisboronic ester **20** was unsuccessful as a Lewis acid catalyst in the Hosomi-Sakurai reaction, or the direct aldol reactions reported herein. Bisboronic acid **10**, was

successful in catalyzing the Conia ene reaction, and provided good yields but no enantioselecvitiy. **10** was also successful in catalyzing the Biginelli reaction, however in poor yield and again, no enantioselecvitiy. Despite these rather dissapointing results, the scope of the investigation was limited. For instance, further aromatic functionalization of **10** may provide a sufficient framework to induce selectivity as a catalyst. Moreover, its tendency to react with alcohols was unexplored. **10** may selectively bind sugar molecules and become useful for the purpose of selective protection or detection of various sugars. Chiral diol **12** may not have induced sufficient enantioselectivity in the addition of diethylzinc to benzaldehyde, however much like **10**, the computational models suggest that futher functionalization may improve upon these results. The computational results also provide insight into the reaction mechanism and represents the first theoretical model of this reaction set. Moreover, it is entirely possible that this ligand is more selective in other enantioselective reactions. As well, still outstanding are the properties and reactivity of **9**. Although its synthesis was unsuccessful, it is certainly still worth persuing. Finally, among the experimental results was the demonstration that computational chemistry is useful to gain valuable chemical insight into reaction mechanisms, predict enantioselecvitiy (or lack thereof), and assist in yield optimization for minor transformations.

6 Concluding Remarks

The research presented within this thesis is nothing short of a culmination of scientific progress. The organic chemistry reported herein demonstrates the acheivements in chemistry since the days of alchemy. The computer hardware, software, and related technologies used to obtain the computational results reported herein are a tribute to computer science, especially considering we only began harnessing electricity in the 1800s. A typical calculation presented herein is computed using $1x10^{10}$ bytes of memory, a number unimaginable just 20 years ago. Furthermore, the entire field of computational chemistry would not exist without the remarkable progress in quantum mechanical descriptions of atoms and molecules, which in turn would not exist had it not been for our thorough understanding of mathmatics and physics. The experimental characterization vital to this work was facilitated by such equipment as nuclear magnetic resonance, electron paramagnetic resonance, high pressure liquid chromatography and mass spectrometry. Without all of these scientific accomplishments, none of this reserach could have taken place. Notwithstanding, this research project clearly demonstrated the ability of computational chemistry to probe reactions in organic chemistry and provide valuable insight to the synthetic organic chemist. Models were able to describe small transformations and complex catalytic reactions. One must wonder just how far computational chemistry can go. We will likely acheive scientific advancements far greater than currently imaginable. One day, quantum chemical computations will be performed on billions of reactant and solvent molecules at once,

accounting entirely for dynamic and statistical effects. Reactions will be optimized entirely *in silico*, without having used any chemical reagents, and by the time a reaction is attempted experimentally it will proceed without any unexpected outcome. Despite the far-fetched nature of this idea, it is my strong belief that scientific discovery will continue to advance to far reaching levels, and those who limit their imagination are simply impeding the progress of science.

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8 Appendix A: Thermochemical and coordinate data for all computed structures

Thermochemical and coordinate data for all computed structures

Section A:

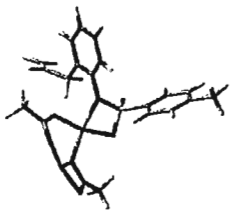
GS-Li

---

opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=373.15

- Thermochemistry -

Zero-point correction= 0.401222 (Hartree/Particle)
Thermal correction to Energy= 0.447933
Thermal correction to Enthalpy= 0.449115
Thermal correction to Gibbs Free Energy= 0.300807
Sum of electronic and zero-point Energies= -1876.001939
Sum of electronic and thermal Energies= -1875.955228
Sum of electronic and thermal Enthalpies= -1875.954046
Sum of electronic and thermal Free Energies= -1876.102354



Cu	-1.10584700	-1.30008400	0.06772200	C	5.12451000	-1.28952100	0.49099300
O	-3.96266400	0.02092700	1.18562200	H	4.16664000	-2.99543500	1.40110000
C	-2.93867600	0.03695800	1.98599600	H	5.76880800	0.45618700	-0.59709100
C	-3.10885800	0.85131200	3.24076000	C	6.46812500	-1.54543800	1.13113400
H	-4.00864700	1.46575800	3.19029900	H	7.28455900	-1.13758300	0.52665800
H	-2.22244100	1.47394400	3.38796100	H	6.52734200	-1.07431800	2.12139700
H	-3.18332500	0.17002500	4.09586500	H	6.64858600	-2.61655500	1.27014500
O	-1.86916200	-0.57145400	1.78312200	C	0.30777200	1.51142900	0.38514400
N	0.04779000	0.26357300	-0.24767700	C	-0.13084100	2.72237400	-0.19900700
S	1.00569200	-0.42587000	-1.35182000	C	0.95354200	1.52402600	1.63132000
C	-1.82261900	3.87003500	-1.71086800	C	0.12499700	3.91532900	0.49037100
H	-2.62813800	3.91796700	-0.97612400	C	1.18609300	2.72202700	2.30336600
C	-1.77398700	4.78282800	-2.68252600	H	1.26543900	0.57744500	2.06252400
H	-0.98764300	4.77349700	-3.43481600	C	0.77407200	3.92401700	1.72528700
H	-2.52285700	5.56553300	-2.77135000	H	-0.19972300	4.85150900	0.04484200
C	-0.84669900	2.73578600	-1.54172200	H	1.68872600	2.71617100	3.26689900
H	-1.37265000	1.77944800	-1.65685600	H	0.95331000	4.86716400	2.23493800
H	-0.10747200	2.75638700	-2.35281100	C	-3.25388300	-2.80818400	-0.54030100
O	1.23386400	0.33751300	-2.58183100	O	-2.07955100	-2.94491700	-0.04052300
O	0.26564700	-1.75461800	-1.45016700	C	-3.93598600	-4.08072600	-0.99867200
C	2.61754500	-0.78979200	-0.65486000	H	-5.00333300	-3.91048300	-1.14928400
C	2.78207400	-1.88963300	0.19242100	H	-3.77151200	-4.88167900	-0.27263400
C	3.68840000	0.05779700	-0.94319800	H	-3.48732200	-4.39903500	-1.94687500
C	4.03276400	-2.13172200	0.75438100	O	-3.82739400	-1.69905100	-0.69053400
H	1.95152500	-2.56146900	0.38268500	H	-3.83634000	-0.63964300	0.39726500
C	4.93222200	-0.19914700	-0.36791000				
H	3.55111400	0.89078000	-1.62397400				

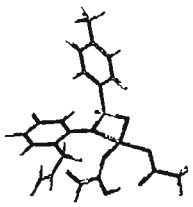
GS-A

---

opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.401222 (Hartree/Particle)
Thermal correction to Energy= 0.450085
Thermal correction to Enthalpy= 0.451299
Thermal correction to Gibbs Free Energy= 0.296804
Sum of electronic and zero-point Energies= -1876.001939
Sum of electronic and thermal Energies= -1875.953075
Sum of electronic and thermal Enthalpies= -1875.951862
Sum of electronic and thermal Free Energies= -1876.106357



Cu	-1.10584700	-1.30008400	0.06772200	C	0.95354200	1.52402600	1.63132000
O	-3.96266400	0.02092700	1.18562200	C	0.12499700	3.91532900	0.49037100
C	-2.93867600	0.03695800	1.98599600	C	1.18609300	2.72202700	2.30336600
C	-3.10885800	0.85131200	3.24076000	H	1.26543900	0.57744500	2.06252400
H	-4.00864700	1.46575800	3.19029900	C	0.77407200	3.92401700	1.72528700
H	-2.22244100	1.47394400	3.38796100	H	-0.19972200	4.85150900	0.04484200
H	-3.18332500	0.17002500	4.09586500	H	1.68872600	2.71617100	3.26689900
O	-1.86916200	-0.57145400	1.78312200	H	0.95331100	4.86716400	2.23493800
N	0.04779000	0.26357300	-0.24767700	C	-3.25388300	-2.80818400	-0.54030100
S	1.00569200	-0.42587000	-1.35182000	O	-2.07955100	-2.94491700	-0.04052300
C	-1.82261900	3.87003500	-1.71086800	C	-3.93598600	-4.08072600	-0.99867200
H	-2.62813800	3.91796700	-0.97612400	H	-5.00333300	-3.91048300	-1.14928400
C	-1.77398600	4.78282800	-2.68252600	H	-3.77151200	-4.88167900	-0.27263400
H	-0.98764200	4.77349700	-3.43481600	H	-3.48732200	-4.39903500	-1.94687500
H	-2.52285600	5.56553300	-2.77135000	O	-3.82739400	-1.69905100	-0.69053400
C	-0.84669900	2.73578600	-1.54172200	H	-3.83634000	-0.63964300	0.39726500
H	-1.37265000	1.77944800	-1.65685600				
H	-0.10747200	2.75638700	-2.35281100				
O	1.23386400	0.33751300	-2.58183100				
O	0.26564700	-1.75461800	-1.45016700				
C	2.61754500	-0.78979200	-0.65486000				
C	2.78207400	-1.88963300	0.19242100				
C	3.68840000	0.05779700	-0.94319800				
C	4.03276400	-2.13172200	0.75438100				
H	1.95152500	-2.56146900	0.38268500				
C	4.93222200	-0.19914800	-0.36791000				
H	3.55111400	0.89078000	-1.62397400				
C	5.12451000	-1.28952200	0.49099300				
H	4.16664000	-2.99543500	1.40110000				
H	5.76880800	0.45618600	-0.59709100				
C	6.46812500	-1.54543900	1.13113400				
H	7.28455900	-1.13758400	0.52665800				
H	6.52734200	-1.07431900	2.12139700				
H	6.64858600	-2.61655600	1.27014500				
C	0.30777200	1.51142900	0.38514400				
C	-0.13084100	2.72237400	-0.19900700				

GS-B

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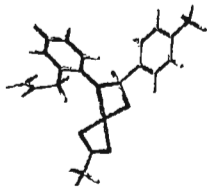
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.338049 (Hartree/Particle)
Thermal correction to Energy= 0.378466
Thermal correction to Enthalpy= 0.379679
Thermal correction to Gibbs Free Energy= 0.245903
Sum of electronic and zero-point Energies= -1646.960806
Sum of electronic and thermal Energies= -1646.920389
Sum of electronic and thermal Enthalpies= -1646.919176
Sum of electronic and thermal Free Energies= -1647.052952



Cu	-1.15767200	-1.67450000	-0.12899300	H	5.16129900	1.76560100	-0.47220300
N	-0.29295500	0.07834300	0.05570300	C	6.46929400	-0.31835500	0.72705500
S	0.69083700	-0.09317100	-1.21410600	H	7.07914000	0.47544800	0.28477800
C	-3.59053900	2.75790100	-0.95208400	H	6.50176300	-0.19011300	1.81714300
H	-4.27376600	2.54759600	-0.12771900	H	6.94420000	-1.27927300	0.50076200
C	-3.95935400	3.61866500	-1.90220000	C	-0.49027200	1.30359700	0.75487100
H	-3.30569100	3.85904600	-2.73843800	C	-1.44275300	2.25424200	0.32144800
H	-4.92935700	4.10876400	-1.88605200	C	0.25948400	1.53487500	1.91751000
C	-2.28119300	2.01506600	-0.92535700	C	-1.58262800	3.42972500	1.06930900
H	-2.48190200	0.93721400	-0.99957900	C	0.10001300	2.71028900	2.64776600
H	-1.69059900	2.26278000	-1.81660400	H	0.96695100	0.77409300	2.23403600
O	0.62097900	0.94270500	-2.24930700	C	-0.82287100	3.66362300	2.21637300
O	0.28149000	-1.51965400	-1.58487000	H	-2.30301300	4.17298600	0.73995000
C	2.39825300	-0.18498200	-0.68268800	H	0.69020600	2.87828600	3.54449000
C	2.89276000	-1.36055700	-0.10899400	H	-0.95824300	4.58670500	2.77391700
C	3.20850400	0.94349300	-0.81623600	C	-3.84855100	-4.06807000	1.22448600
C	4.21221100	-1.39554700	0.33186500	H	-3.43408400	-5.07375900	1.33674700
H	2.26169500	-2.23999100	-0.03797200	H	-4.25442800	-3.71180200	2.17290900
C	4.52648000	0.88996200	-0.36337900	H	-4.65688100	-4.12314800	0.48618000
H	2.81589300	1.83888100	-1.28554300	C	-2.78880900	-3.13306000	0.71813400
C	5.04787500	-0.27249800	0.21921900	O	-2.65570900	-1.95719800	1.19550900
H	4.60426700	-2.31307300	0.76393800	O	-1.99864500	-3.47880500	-0.22342400

GS-C

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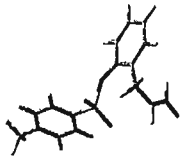
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.284514 (Hartree/Particle)
Thermal correction to Energy= 0.314461
Thermal correction to Enthalpy= 0.315674

Thermal correction to Gibbs Free Energy= 0.211669
Sum of electronic and zero-point Energies= -1222.289768
Sum of electronic and thermal Energies= -1222.259821
Sum of electronic and thermal Enthalpies= -1222.258608
Sum of electronic and thermal Free Energies= -1222.362613



N	0.42186300	0.60210700	-0.11454000	H	-2.27819400	0.65576300	2.09861000
S	-0.35378800	-0.76022800	0.48125300	C	-4.71314100	0.43688600	-0.29588900
C	3.03534900	-2.29379200	-0.32826600	H	-4.45030800	-0.53189900	-2.20416100
H	2.77219700	-3.31615800	-0.06090400	H	-4.63910200	1.30785200	1.67535400
C	3.48565300	-2.03858900	-1.55627800	C	-6.15995700	0.79794500	-0.53701500
H	3.75159300	-1.03767200	-1.88565100	H	-6.43575500	1.72008900	-0.01472100
H	3.59140000	-2.83415400	-2.28837300	H	-6.36683300	0.93527000	-1.60346700
C	2.85681200	-1.29769700	0.80381200	H	-6.82882400	0.00593500	-0.17449900
H	1.94612800	-1.53557400	1.35544300	C	1.73408400	0.91482600	-0.06843200
H	3.67337400	-1.45218500	1.52494300	C	2.88561500	0.15116700	0.37645100
O	-0.17190500	-0.83916000	1.94209700	C	1.95881200	2.25723600	-0.54354100
O	-0.06097300	-1.93145500	-0.35812700	C	4.12639500	0.78661600	0.35059400
C	-2.05058800	-0.28092700	0.17416900	C	3.20702200	2.84014800	-0.55486500
C	-2.65175700	-0.62896700	-1.03561300	H	1.07884200	2.79622700	-0.87747900
C	-2.75831200	0.41148400	1.15707400	C	4.30758600	2.10071100	-0.09627800
C	-3.97754400	-0.26401800	-1.26234300	H	4.99345600	0.22341700	0.68608700
H	-2.08974800	-1.18427900	-1.77893700	H	3.33417100	3.85866900	-0.90954000
C	-4.08324100	0.76752400	0.91280200	H	5.30146700	2.53919200	-0.09103600

GS-D

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opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.388669 (Hartree/Particle)
Thermal correction to Energy= 0.437589
Thermal correction to Enthalpy= 0.438802
Thermal correction to Gibbs Free Energy= 0.285745
Sum of electronic and zero-point Energies= -1875.493255
Sum of electronic and thermal Energies= -1875.444335
Sum of electronic and thermal Enthalpies= -1875.443122
Sum of electronic and thermal Free Energies= -1875.596179

Cu	-1.76120500	-0.71854600	-0.13946500	H	-5.07681000	-2.32511500	-2.59373300
O	-3.87795700	0.22625700	-1.20376900	H	-5.97654000	-0.82574600	-2.20770600
C	-4.05540500	-1.00318100	-1.22617100	O	-3.19812900	-1.85712400	-0.76879000
C	-5.33021300	-1.60887500	-1.80434000	N	-0.20188600	0.55376200	-0.05689500
H	-5.86418800	-2.16137000	-1.02268900	S	0.52541900	0.14762900	-1.43007300

C	0.39949400	4.31091700	-1.19154100
H	1.13780800	3.73049300	-1.74204100
C	0.33052600	5.63478800	-1.35113400
H	-0.40619600	6.23819500	-0.82211500
H	0.99792700	6.16658100	-2.02588200
C	-0.49314800	3.50267400	-0.28465300
H	-1.25373100	4.16166300	0.15608100
H	-1.01837500	2.74318200	-0.87196200
O	0.98396500	1.26231500	-2.28241700
O	-0.48853800	-0.80599500	-1.99911300
C	2.00582900	-0.82620200	-1.07635200
C	1.92788000	-1.91741600	-0.20300300
C	3.20723500	-0.49676900	-1.70163200
C	3.07423800	-2.67304800	0.03258100
H	0.99716600	-2.16187400	0.30526300
C	4.34434500	-1.26850500	-1.45348800
H	3.23893700	0.35357900	-2.37402000
C	4.29652000	-2.36487200	-0.58520800
H	3.01503900	-3.51910500	0.71428400
H	5.28198600	-1.01240300	-1.94316200
C	5.53113000	-3.18964900	-0.30021200
H	5.89478300	-3.02491800	0.72308200
H	5.32770700	-4.26313800	-0.39787000
H	6.34812100	-2.93793400	-0.98508400
C	0.38208800	1.40418600	0.91793500
C	0.26868400	2.81049900	0.83660300
C	1.02692000	0.82602100	2.02602300
C	0.85241900	3.58793400	1.84678800
C	1.58728700	1.61828500	3.02455400
H	1.05680800	-0.25685900	2.09093300
C	1.50970500	3.00999300	2.93086700
H	0.78134800	4.67140500	1.77194100
H	2.08125100	1.15001800	3.87310900
H	1.94792100	3.64028600	3.70182900
C	-1.45801200	-1.75442400	2.35036200
O	-2.19312000	-0.86718500	1.77398500
C	-1.78673900	-1.96709000	3.83069700
H	-1.60810100	-1.03747700	4.38319500
H	-1.16999900	-2.76639300	4.24890200
H	-2.84739500	-2.21470300	3.94639500
O	-0.54231100	-2.40333300	1.81549

TS-A

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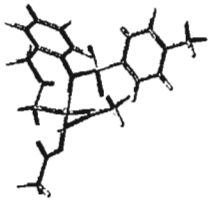
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.400984 (Hartree/Particle)
Thermal correction to Energy= 0.448461
Thermal correction to Enthalpy= 0.449675
Thermal correction to Gibbs Free Energy= 0.301755
Sum of electronic and zero-point Energies= -1875.979746
Sum of electronic and thermal Energies= -1875.932268
Sum of electronic and thermal Enthalpies= -1875.931054
Sum of electronic and thermal Free Energies= -1876.078974



Cu	-1.65125000	-0.23486700	-0.60204000
O	-3.84453400	-1.27553800	1.01469800
C	-4.03310700	-1.54050300	-0.20196600
C	-5.34455900	-2.18479600	-0.61768200
H	-5.50508600	-2.10452300	-1.69436800
H	-6.17144000	-1.72302300	-0.07092500
H	-5.32115900	-3.24563800	-0.34075900
O	-3.18245500	-1.31613800	-1.12997100
N	-0.08545900	1.06687900	-0.45238700
S	1.10788400	0.97310300	-1.65799400
C	-1.48294300	2.36024000	-1.17339000
H	-1.04353000	2.46608900	-2.16075700
C	-2.66717500	1.59032300	-1.10091600
H	-3.33608200	1.70893300	-0.25003800
H	-3.11499000	1.22890200	-2.02222500
C	-1.15952700	3.47508900	-0.18806700
H	-0.58484500	4.25159200	-0.70791700
H	-2.09391400	3.93389500	0.15648100
O	1.67737700	2.31196100	-1.87205500
O	0.42586800	0.26870600	-2.75486600
C	2.43000900	-0.07388000	-1.05105400
C	2.31600200	-1.46203900	-1.15579300
C	3.57436200	0.51774600	-0.51107200
C	3.36645400	-2.25997300	-0.70569600

H	1.42481100	-1.90466800	-1.58434600	C	1.13268400	1.76036800	3.02451400
C	4.61153200	-0.29802600	-0.06289000	H	1.36163900	0.08939300	1.66917200
H	3.64899400	1.59832400	-0.45992500	C	0.56817200	3.02434800	3.21549900
C	4.52673800	-1.69497900	-0.15394400	H	-0.64059900	4.59199400	2.35604900
H	3.28896700	-3.34102400	-0.79497400	H	1.70829800	1.29617500	3.82059800
H	5.50459300	0.15827700	0.35704700	H	0.70539700	3.54439100	4.15941700
C	5.67307800	-2.56871500	0.29706700	C	-0.73613200	-2.41261200	1.43172000
H	5.32617000	-3.56094200	0.60350300	O	-0.55662100	-1.78274300	0.37966500
H	6.39795000	-2.71338400	-0.51503200	C	0.33787300	-3.30338900	2.00752700
H	6.21301600	-2.12024500	1.13759400	H	0.03298700	-4.35021500	1.89632800
C	0.21299900	1.68812100	0.79505900	H	0.45078000	-3.10995000	3.07834200
C	-0.36318000	2.95155900	0.98702400	H	1.28236800	-3.14167400	1.48687400
C	0.94748100	1.07985200	1.82015900	O	-1.83528100	-2.39431900	2.13916600
C	-0.18811700	3.61560800	2.20068100	H	-2.58670800	-1.86081700	1.67984700

I-1A

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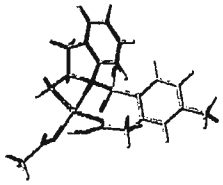
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.401934 (Hartree/Particle)
Thermal correction to Energy= 0.449465
Thermal correction to Enthalpy= 0.450678
Thermal correction to Gibbs Free Energy= 0.304531
Sum of electronic and zero-point Energies= -1875.991666
Sum of electronic and thermal Energies= -1875.944135
Sum of electronic and thermal Enthalpies= -1875.942922
Sum of electronic and thermal Free Energies= -1876.089070



Cu	-1.77850200	0.03957700	-0.35752900	C	1.82824500	-1.70771900	-1.21034800
O	-4.27608900	-1.14379000	0.91798000	C	3.55293800	-0.07183600	-0.67585100
C	-4.36862800	-1.04994400	-0.33742600	C	2.68395900	-2.72503200	-0.79256100
C	-5.72601600	-1.31105300	-0.97015900	H	0.83658200	-1.93407300	-1.58293800
H	-5.74278200	-1.00210700	-2.01674200	C	4.39068700	-1.10457000	-0.26166000
H	-6.50089900	-0.78429000	-0.40509500	H	3.88143500	0.96116300	-0.65204100
H	-5.94975300	-2.38237600	-0.90646300	C	3.97328900	-2.44295300	-0.31522800
O	-3.40889400	-0.76262100	-1.12488900	H	2.34835000	-3.75750300	-0.84953100
N	0.07857300	1.27728300	-0.44579500	H	5.38739800	-0.86803100	0.10192200
S	1.23299900	0.92664800	-1.75732900	C	4.90469600	-3.55804300	0.09551500
C	-0.83426600	2.46754300	-0.88833100	H	4.35195200	-4.43073100	0.45792600
H	-0.75128300	2.56055600	-1.97174400	H	5.51475200	-3.88879600	-0.75544900
C	-2.22257300	2.01468800	-0.50721600	H	5.59352800	-3.23656100	0.88348100
H	-2.54655400	2.31296800	0.49481800	C	0.66639000	1.70932600	0.80252200
H	-2.99306000	2.17564500	-1.26002400	C	0.48692100	3.08055700	1.01494600
C	-0.25468800	3.69671900	-0.14633100	C	1.27898600	0.88950800	1.74800100
H	0.42909900	4.26396000	-0.79003300	C	0.95489100	3.66015200	2.19085000
H	-1.05716900	4.37085400	0.17036900	C	1.75410100	1.48462600	2.92059200
O	2.06757400	2.11615500	-1.96914600	H	1.36386700	-0.17770700	1.58144500
O	0.38436300	0.40133600	-2.83032300	C	1.59769200	2.85678900	3.13927600
C	2.27368400	-0.38576500	-1.14158100	H	0.81794200	4.72270500	2.37376400

H	2.23623700	0.86903100	3.67482500	H	-0.62705300	-4.31162300	2.10377400
H	1.96329400	3.30071700	4.06104500	H	-0.11713300	-3.03612100	3.20705300
C	-1.20566400	-2.33611300	1.50244600	H	0.73912000	-3.24294600	1.64982700
O	-0.83741100	-1.57195100	0.59060500	O	-2.40407500	-2.39718800	1.99518800
C	-0.22980800	-3.29270600	2.14797600	H	-3.11204700	-1.78039100	1.50805800

I-2A

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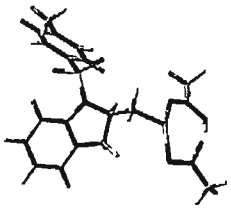
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.403376 (Hartree/Particle)
Thermal correction to Energy= 0.451379
Thermal correction to Enthalpy= 0.452592
Thermal correction to Gibbs Free Energy= 0.300389
Sum of electronic and zero-point Energies= -1875.989313
Sum of electronic and thermal Energies= -1875.941309
Sum of electronic and thermal Enthalpies= -1875.940096
Sum of electronic and thermal Free Energies= -1876.092299



Cu	-2.77557900	-0.41551800	0.72540600	H	4.93720800	-0.84859200	-1.58757000
O	-4.85344500	-0.47485500	1.20777400	C	5.33564200	-1.84255600	1.66329300
C	-4.70623300	0.65675200	1.80164000	H	3.71434000	-2.02490700	3.07669200
C	-5.90715900	1.33464600	2.41243800	H	6.69992200	-1.56260700	0.01992000
H	-5.64383800	2.32165200	2.79536900	C	6.40004000	-2.25694200	2.65144800
H	-6.29135600	0.71457000	3.23001800	H	6.57340200	-1.47155900	3.39858500
H	-6.70441200	1.41906600	1.66699500	H	6.10725500	-3.16119100	3.19746800
O	-3.55658000	1.16951500	1.88455100	H	7.35377800	-2.45616700	2.15327200
N	1.19924800	0.58583100	-0.55675500	C	1.60139400	1.94659500	-0.56347400
S	2.09145500	-0.61631800	-1.34868100	C	0.48176900	2.78645900	-0.55282700
C	-0.31806900	0.48183500	-0.53057300	C	2.89647800	2.46503800	-0.53161400
H	-0.62987600	-0.06481600	-1.42186500	C	0.64688200	4.16579900	-0.50609100
C	-0.78820100	-0.25755300	0.70491300	C	3.04850700	3.85459200	-0.49799000
H	-0.45987800	-1.30195100	0.71421100	H	3.76496600	1.81698700	-0.54163600
H	-0.53135800	0.26165000	1.63474000	C	1.93925300	4.70329500	-0.48147900
C	-0.78655900	1.96855800	-0.58799600	H	-0.22112800	4.82081700	-0.49406600
H	-1.36556100	2.16458400	-1.49998200	H	4.05047700	4.27495100	-0.48087800
H	-1.44195600	2.19239800	0.26188700	H	2.07853000	5.78015100	-0.45004900
O	2.78113100	-0.07135000	-2.52337000	C	-4.07788100	-1.93297400	-1.54157700
O	1.17196300	-1.75106000	-1.48849400	O	-3.03072700	-1.58990700	-0.97597200
C	3.35505000	-1.04025400	-0.14675600	C	-4.06234300	-2.74940700	-2.80476800
C	2.99794300	-1.37446800	1.16272200	H	-4.72345700	-2.29879700	-3.55096600
C	4.68313100	-1.10860400	-0.56568100	H	-4.44866600	-3.75179700	-2.58808200
C	3.98856300	-1.76889200	2.05596700	H	-3.04460100	-2.82474900	-3.18769200
H	1.96140200	-1.31252100	1.47761800	O	-5.28805500	-1.64149400	-1.11156100
C	5.66363700	-1.50881900	0.34402500	H	-5.24676300	-1.14225700	-0.24173600

I-3

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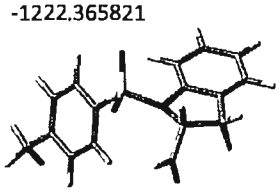
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.285077 (Hartree/Particle)
Thermal correction to Energy= 0.314376
Thermal correction to Enthalpy= 0.315590
Thermal correction to Gibbs Free Energy= 0.214831
Sum of electronic and zero-point Energies= -1222.295575
Sum of electronic and thermal Energies= -1222.266276
Sum of electronic and thermal Enthalpies= -1222.265062
Sum of electronic and thermal Free Energies= -1222.365821



N	1.03533000	-0.67747700	-0.03467100	H	-1.98051200	1.04476300	2.05905900
S	-0.15119000	-0.97715200	1.15332700	C	-4.00559600	0.71159700	-0.67989300
C	1.95130900	-1.83741600	-0.41263700	H	-3.62274500	-0.65706300	-2.30544200
H	2.27145300	-2.32773500	0.51208400	H	-4.08850600	1.94420900	1.08431200
C	1.28812400	-2.82407900	-1.30599800	C	-5.28517600	1.24586200	-1.27836200
H	1.08796000	-2.55860900	-2.34057000	H	-5.72831400	2.02307100	-0.64861700
H	0.89108100	-3.75338400	-0.91743800	H	-5.10983500	1.67664000	-2.27175200
C	3.15931300	-1.11220600	-1.07485700	H	-6.02860300	0.44843000	-1.40046900
H	4.10407100	-1.58422600	-0.78537700	C	1.78233000	0.53367300	-0.04419300
H	3.08541600	-1.18599500	-2.16848200	C	3.03721100	0.32338000	-0.62871500
O	0.12711500	-0.20881700	2.37108900	C	1.39199100	1.80170500	0.38764100
O	-0.28083100	-2.43632700	1.20686500	C	3.92722500	1.38020600	-0.77724400
C	-1.63110600	-0.28954000	0.41181300	C	2.29906000	2.85561500	0.23791600
C	-2.08778500	-0.78439200	-0.81371200	H	0.42573000	1.97126500	0.84589000
C	-2.34637200	0.68610900	1.10293600	C	3.55672500	2.65555700	-0.33533900
C	-3.26620900	-0.27849400	-1.35034700	H	4.90186900	1.21590200	-1.23061100
H	-1.52258800	-1.54923500	-1.33673300	H	2.01422100	3.84651600	0.58114500
C	-3.52873000	1.18166200	0.54883700	H	4.24688100	3.48792900	-0.43823500

2

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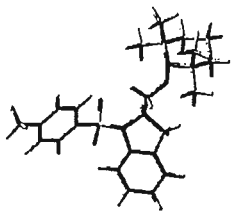
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.556596 (Hartree/Particle)
Thermal correction to Energy= 0.605086
Thermal correction to Enthalpy= 0.606299
Thermal correction to Gibbs Free Energy= 0.463938
Sum of electronic and zero-point Energies= -1705.801809
Sum of electronic and thermal Energies= -1705.753320

Sum of electronic and thermal Enthalpies= -1705.752107
Sum of electronic and thermal Free Energies= -1705.894468



N	1.22959600	0.82085600	-0.51712900	H	0.15292100	5.07142100	0.40383600
S	2.23154500	-0.07294500	-1.57900700	H	4.06891200	3.80569200	1.67294300
C	-0.22215300	0.96666800	-0.87300100	H	2.32354500	5.55978200	1.52299900
H	-0.39879800	0.55940600	-1.86817600	C	-5.23968900	0.77005100	0.22327600
C	-1.03789800	0.15617600	0.13897700	C	-5.85078500	-0.26052000	-0.73541800
H	-0.69294100	-0.88232300	0.13510900	C	-4.74851500	-1.04386100	-1.46030000
H	-0.90299000	0.55978200	1.15214800	C	-3.73742600	-1.70265300	-0.49256500
C	-0.49359800	2.49223000	-0.81544700	C	-4.23250200	0.14857100	1.22089600
H	-0.55045900	2.92261800	-1.82404200	H	-5.18638600	-1.81716900	-2.10500900
H	-1.45026800	2.69759900	-0.32581600	H	-6.51311200	-0.94579200	-0.18972100
O	3.14909100	0.81338200	-2.30183500	H	-6.48608700	0.25029800	-1.46988800
O	1.32034900	-0.96621500	-2.30324000	H	-4.71325800	1.53200000	-0.36524800
C	3.21763000	-1.06207600	-0.45465200	H	-6.02793400	1.29009000	0.78358400
C	2.59424900	-1.97758500	0.39888100	H	-4.19736700	-0.35802800	-2.11566100
C	4.60664500	-0.95817400	-0.50178700	N	-3.20412700	-0.70687900	0.51605300
C	3.37774100	-2.78131300	1.21930500	O	-2.39923400	0.22969800	-0.26678000
H	1.51243300	-2.05754100	0.41931800	C	-3.49469800	1.27301200	1.97178700
C	5.37758300	-1.77472400	0.32870900	H	-4.22208200	1.86660800	2.53662900
H	5.06904800	-0.25048900	-1.18134600	H	-2.77196100	0.85872000	2.68363100
C	4.78053800	-2.69403700	1.19862400	H	-2.97093200	1.94342300	1.28918100
H	2.89567000	-3.49206300	1.88631300	C	-4.94975600	-0.68629500	2.30563500
H	6.46119700	-1.69628400	0.29410900	H	-4.22743400	-1.29569600	2.85774200
C	5.61408100	-3.57666900	2.09693600	H	-5.43154700	-0.00506400	3.01552900
H	6.68429000	-3.41401100	1.93810500	H	-5.72956400	-1.34183200	1.91828700
H	5.39828600	-3.38282700	3.15499100	C	-4.36143200	-2.90993900	0.24383100
H	5.40429500	-4.63780900	1.91544900	H	-4.41476500	-3.75628500	-0.44961200
C	1.68722400	2.05469600	0.03678200	H	-3.73588000	-3.20645100	1.09156100
C	0.69734400	3.03948100	-0.06363300	H	-5.37478600	-2.73597500	0.60638400
C	2.90694300	2.30824900	0.66089300	C	-2.55399500	-2.26956800	-1.30071000
C	0.91821700	4.30231600	0.47457800	H	-2.93310100	-3.00648200	-2.01744200
C	3.12302700	3.58659100	1.18511100	H	-2.02498200	-1.49902500	-1.86262500
H	3.66848100	1.54095500	0.74293800	H	-1.84010100	-2.78138500	-0.64553100
C	2.14005900	4.57579100	1.10092700				

TS-B

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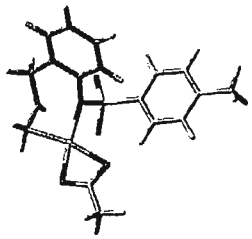
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.337937 (Hartree/Particle)
Thermal correction to Energy= 0.376832
Thermal correction to Enthalpy= 0.378046
Thermal correction to Gibbs Free Energy= 0.252531
Sum of electronic and zero-point Energies= -1646.942067

Sum of electronic and thermal Energies= -1646.903172
Sum of electronic and thermal Enthalpies= -1646.901959
Sum of electronic and thermal Free Energies= -1647.027473



Cu	1.81459900	1.02062400	-0.00684800	C	-3.06397000	-0.89758600	-0.89894300
O	0.62302300	2.59518000	0.84943700	C	-3.37635300	1.60232300	0.30500600
C	1.70248400	3.25626400	0.85893100	H	-1.32281200	1.97153800	-0.23712400
C	1.75131300	4.68265300	1.34649800	C	-4.28241200	-0.54246000	-0.32094500
H	0.78011800	4.99051600	1.73768900	H	-2.92486600	-1.86283600	-1.37294600
H	2.03965000	5.33919900	0.51833100	C	-4.45899500	0.70787000	0.28648500
H	2.51745500	4.78142600	2.12209800	H	-3.49313300	2.57448400	0.77771500
O	2.78009400	2.70369500	0.43864000	H	-5.10813500	-1.24929400	-0.34294900
N	0.68006800	-0.60314600	-0.38509800	C	-5.78780500	1.09880900	0.88820600
S	-0.45716500	-0.43267200	-1.63850300	H	-5.65559600	1.65838300	1.82073800
C	2.43425200	-1.18873000	-1.25850400	H	-6.35406100	1.74293800	0.20253000
H	2.11059300	-1.03824300	-2.28460700	H	-6.40673800	0.22147400	1.10082800
C	3.34749900	-0.23274700	-0.75001300	C	0.53362800	-1.63906100	0.58410200
H	3.95845500	-0.48250800	0.11629100	C	1.42910200	-2.70975100	0.45126500
H	3.77416300	0.49437500	-1.43847200	C	-0.36231000	-1.59041600	1.65845300
C	2.35147200	-2.61827900	-0.74434200	C	1.41890700	-3.74255200	1.38756400
H	1.97687200	-3.26328200	-1.54854800	C	-0.37768500	-2.63878100	2.58010700
H	3.35867500	-2.96532800	-0.48445100	H	-1.03150400	-0.74354300	1.76761200
O	-0.64454100	-1.72935000	-2.30553700	C	0.50806200	-3.71129400	2.44672100
O	0.05926900	0.71997000	-2.39400000	H	2.11816200	-4.56968200	1.29252100
C	-2.01008000	0.01673400	-0.87041600	H	-1.07523200	-2.60991300	3.41249700
C	-2.15260200	1.27345700	-0.27224900	H	0.49892300	-4.51768500	3.17468200

I-1B

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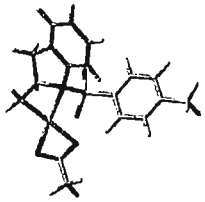
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.339740 (Hartree/Particle)
Thermal correction to Energy= 0.378694
Thermal correction to Enthalpy= 0.379907
Thermal correction to Gibbs Free Energy= 0.255549
Sum of electronic and zero-point Energies= -1646.953593
Sum of electronic and thermal Energies= -1646.914639
Sum of electronic and thermal Enthalpies= -1646.913426
Sum of electronic and thermal Free Energies= -1647.037783



Cu	2.05427700	0.79340400	0.05533300	C	2.22078200	4.53709300	1.17271300
O	1.03642500	2.49498100	0.66609800	H	1.59886600	4.69953200	2.05838100
C	2.16514700	3.08307900	0.76891600	H	1.80689900	5.14983400	0.36368700

H	3.24797600	4.84799300	1.37047100
O	3.23216900	2.44300500	0.51655500
N	0.70161500	-0.83161400	-0.45330400
S	-0.47044700	-0.47921700	-1.75477200
C	1.94264300	-1.57019100	-1.06313900
H	1.91204300	-1.42313200	-2.14347100
C	3.11429900	-0.82858300	-0.45890000
H	3.50477500	-1.26990500	0.46349500
H	3.91545000	-0.58195300	-1.15723700
C	1.73970400	-3.05207600	-0.66873000
H	1.27337500	-3.62036200	-1.48308200
H	2.69984600	-3.52312700	-0.43461000
O	-0.88260200	-1.75117300	-2.36113300
O	0.21566900	0.54253900	-2.55049400
C	-1.87601700	0.23779200	-0.92436300
C	-1.79784200	1.53580200	-0.40892900
C	-3.05483100	-0.50785400	-0.85706400
C	-2.93000500	2.07683900	0.19549200
H	-0.87349400	2.10220100	-0.44769600
C	-4.17609500	0.06118500	-0.25673600
H	-3.08567200	-1.50842500	-1.27339900
C	-4.13310900	1.35713500	0.27635300
H	-2.87683200	3.08037800	0.60985900
H	-5.09845900	-0.51116600	-0.20146900
C	-5.35827700	1.97828800	0.90285000
H	-5.09998100	2.56331400	1.79213600
H	-5.85275600	2.66077900	0.19917100
H	-6.09057800	1.21857700	1.19331000
C	0.23951700	-1.70027600	0.60721000
C	0.81983300	-2.97086700	0.52500200
C	-0.61009900	-1.34257700	1.65240000
C	0.52378600	-3.92458800	1.49460500
C	-0.90636600	-2.31153400	2.61556800
H	-1.01987900	-0.34113000	1.72185300
C	-0.34895700	-3.59137500	2.53631200
H	0.97056900	-4.91424000	1.44800500
H	-1.56609100	-2.05881400	3.44063000
H	-0.58221400	-4.32885500	3.29922600

I-2B

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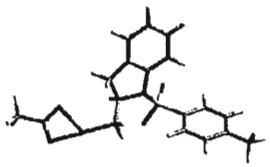
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.339828 (Hartree/Particle)
Thermal correction to Energy= 0.364989
Thermal correction to Enthalpy= 0.365933
Thermal correction to Gibbs Free Energy= 0.278639
Sum of electronic and zero-point Energies= -1646.937915
Sum of electronic and thermal Energies= -1646.912754
Sum of electronic and thermal Enthalpies= -1646.911810
Sum of electronic and thermal Free Energies= -1646.999104



Cu	3.23599800	-1.37101800	-0.54345300
O	5.19664900	-1.80125100	-0.53723100
C	5.42387000	-0.71479800	0.08982000
C	6.82252600	-0.34869600	0.51052200
H	7.53127600	-0.63171600	-0.27191600
H	7.07837600	-0.91301600	1.41493600
H	6.89512000	0.71806100	0.72991600
O	4.44337900	0.04935000	0.37915000
N	-0.50987300	0.56342600	0.20558100
S	-1.40990200	-0.23140700	1.41707100
C	0.99075600	0.31284200	0.17242100
H	1.34796900	0.26471900	1.20539500
C	1.33192100	-0.97486500	-0.54856900
H	0.90930400	-1.85436000	-0.05015300
H	1.04028900	-0.94336200	-1.60737600
C	1.55045900	1.58455500	-0.52425700
H	2.44848900	1.94649700	-0.01467200
H	1.84437400	1.34476200	-1.55597100
O	-1.88248400	0.71421600	2.43345500
O	-0.59574500	-1.38786700	1.80832200
C	-2.84846200	-0.81017800	0.51618500
C	-2.69085600	-1.58659800	-0.63550200
C	-4.11611700	-0.54386400	1.03193600
C	-3.82004100	-2.08397900	-1.27732200
H	-1.69887700	-1.78856700	-1.02596000
C	-5.23796500	-1.05332100	0.37554200
H	-4.21539200	0.05237000	1.93263500
C	-5.11047900	-1.82539700	-0.78514700
H	-3.70122600	-2.68497400	-2.17574900
H	-6.22742700	-0.84739200	0.77584800
C	-6.32618700	-2.35664500	-1.50661300
H	-6.51654900	-1.79085800	-2.42799000

H	-6.19290500	-3.40562100	-1.79454800	C	-1.99716500	3.95791300	-0.44485400
H	-7.22390500	-2.28682000	-0.88482700	H	-2.89765000	2.12621000	0.25725600
C	-0.76742900	1.93150400	-0.09879100	C	-0.82964600	4.60525200	-0.85553100
C	0.40767100	2.56730900	-0.51546400	H	1.29323500	4.39913200	-1.21982200
C	-1.98517800	2.61176400	-0.06663800	H	-2.93542000	4.50514600	-0.41310100
C	0.38075200	3.90386200	-0.89648200	H	-0.86044200	5.65228800	-1.14308500

TS-D

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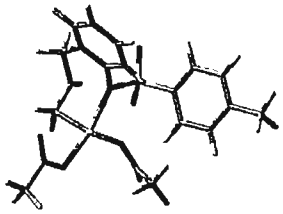
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.388059 (Hartree/Particle)
Thermal correction to Energy= 0.435410
Thermal correction to Enthalpy= 0.436623
Thermal correction to Gibbs Free Energy= 0.289817
Sum of electronic and zero-point Energies= -1875.451013
Sum of electronic and thermal Energies= -1875.403662
Sum of electronic and thermal Enthalpies= -1875.402449
Sum of electronic and thermal Free Energies= -1875.549255



Cu	1.54830500	0.62739000	-0.47510100	H	-3.56956600	-2.04706700	-0.01672100
O	3.89772700	0.62939900	1.14429700	C	-4.59544300	1.17925600	0.48743300
C	3.92478300	1.61463200	0.39284500	H	-3.51741000	2.90946800	-0.23364100
C	5.06152700	2.64019300	0.50346300	H	-5.40004500	-0.73697000	1.06136000
H	4.65345600	3.60465700	0.82796200	C	-5.70226400	1.98447100	1.12916100
H	5.52668300	2.79962700	-0.47580900	H	-5.29900400	2.74730500	1.80647900
H	5.81251200	2.30282300	1.22263200	H	-6.30191200	2.51163700	0.37522300
O	3.05836200	1.89900400	-0.52199400	H	-6.38039500	1.34648900	1.70609500
N	0.15666100	-1.05986100	-0.59701200	C	0.22166800	-1.77922400	0.63274600
S	-1.25037400	-1.24394500	-1.51678800	C	1.08356800	-2.88444100	0.60657700
C	1.64201300	-1.83876200	-1.58513300	C	-0.40887400	-1.39184600	1.81917600
H	1.11545500	-1.94929800	-2.52866800	C	1.28300200	-3.63440100	1.76414700
C	2.64844100	-0.83783000	-1.54600500	C	-0.21714400	-2.16118700	2.96828600
H	3.47257000	-0.94108800	-0.84477000	H	-1.00361700	-0.48594700	1.83754800
H	2.85397000	-0.28270700	-2.45850100	C	0.61902800	-3.28113000	2.94237700
C	1.73774700	-3.11014200	-0.73778700	H	1.95884500	-4.48707100	1.75113400
H	1.23535400	-3.93356700	-1.26287400	H	-0.70517900	-1.86986200	3.89519400
H	2.79115300	-3.38852600	-0.61518700	H	0.77412100	-3.86537800	3.84640000
O	-1.67893600	-2.65732500	-1.48998300	C	0.03856600	2.84241700	0.30076300
O	-0.96331100	-0.60976400	-2.81097500	O	0.47414000	1.72679600	0.77531900
C	-2.54567100	-0.29309300	-0.71496300	C	-0.29806900	3.88764900	1.37301300
C	-2.52024400	1.10170800	-0.79234100	H	-0.97891400	3.45854000	2.11739500
C	-3.57377300	-0.96310700	-0.05205500	H	-0.75049800	4.77553400	0.92262100
C	-3.54543300	1.82321200	-0.18568700	H	0.61853000	4.17401300	1.90193700
H	-1.70508700	1.62449300	-1.28512200	O	-0.13150100	3.11085600	-0.89984900
C	-4.59415300	-0.22020700	0.54405300				

I-1D

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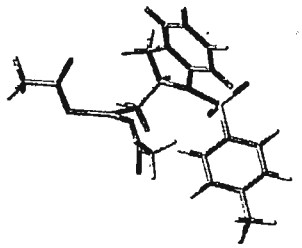
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.390007 (Hartree/Particle)
Thermal correction to Energy= 0.437713
Thermal correction to Enthalpy= 0.438926
Thermal correction to Gibbs Free Energy= 0.289660
Sum of electronic and zero-point Energies= -1875.477276
Sum of electronic and thermal Energies= -1875.429570
Sum of electronic and thermal Enthalpies= -1875.428357
Sum of electronic and thermal Free Energies= -1875.577623



Cu	-2.13006100	-1.16929100	-0.16783600	H	4.63599500	1.44045900	-0.88605300
O	-4.67201300	0.25951300	0.02565900	C	4.47764800	-1.87781300	-0.06344000
C	-4.81577100	-0.80372000	-0.59456300	H	2.61979600	-3.00842600	-0.00506400
C	-6.20411600	-1.22164000	-1.09301300	H	6.09287400	-0.45413600	-0.18807800
H	-6.45972600	-2.21308500	-0.70219300	C	5.35159400	-3.03119200	0.37334800
H	-6.19596000	-1.30003100	-2.18660300	H	4.99441600	-3.46625900	1.31481000
H	-6.96018400	-0.49580000	-0.78329600	H	5.34700800	-3.83734000	-0.37153900
O	-3.87896200	-1.64564100	-0.89100000	H	6.39067900	-2.71667200	0.51924100
N	0.40191800	1.43966700	-0.61751900	C	0.22903400	1.97119000	0.68532300
S	1.84172700	1.61208700	-1.46746400	C	-1.09868300	2.37977500	0.86562200
C	-0.92145500	1.40858400	-1.35332200	C	1.16865900	2.07519300	1.71043200
H	-0.77644700	1.96216100	-2.28814900	C	-1.50451400	2.88647700	2.09419500
C	-1.37935200	-0.00282400	-1.67336400	C	0.74883800	2.60170100	2.93660700
H	-2.25863900	0.03255200	-2.32599700	H	2.19664900	1.76278700	1.56681300
H	-0.59165600	-0.59109100	-2.15534200	C	-0.57463200	3.00001500	3.13568600
C	-1.88393900	2.19224900	-0.41022900	H	-2.53778900	3.19185400	2.24114100
H	-2.15304300	3.16706200	-0.84189100	H	1.46868600	2.69087400	3.74695500
H	-2.81093800	1.62842100	-0.25447900	H	-0.88497000	3.39492600	4.09992100
O	2.54252600	2.84793800	-1.08363100	C	-0.20595200	-2.45842100	1.38318000
O	1.51587200	1.37922200	-2.88053600	O	-1.06010500	-1.48848300	1.40723400
C	2.84521200	0.24848400	-0.86856600	C	0.45420800	-2.73226500	2.73850400
C	2.27677400	-1.00392600	-0.62776100	H	1.14859700	-1.91529600	2.96945400
C	4.21711100	0.45499700	-0.71212700	H	1.00558600	-3.67610600	2.71728100
C	3.09469600	-2.05483500	-0.21921000	H	-0.29773900	-2.75215900	3.53385500
H	1.20967400	-1.17043700	-0.71889400	O	0.11693600	-3.12211600	0.38585200
C	5.02360700	-0.61191900	-0.31417300				

I-1C

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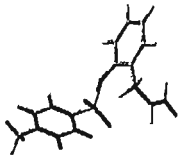
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.284514 (Hartree/Particle)
Thermal correction to Energy= 0.314461
Thermal correction to Enthalpy= 0.315674
Thermal correction to Gibbs Free Energy= 0.211669
Sum of electronic and zero-point Energies= -1222.289768
Sum of electronic and thermal Energies= -1222.259821
Sum of electronic and thermal Enthalpies= -1222.258608
Sum of electronic and thermal Free Energies= -1222.362613



N	0.42186300	0.60210700	-0.11454000	C	-4.71314100	0.43688600	-0.29588900
S	-0.35378800	-0.76022800	0.48125300	H	-4.45030800	-0.53189900	-2.20416100
C	3.03534900	-2.29379200	-0.32826600	H	-4.63910200	1.30785200	1.67535400
H	2.77219700	-3.31615800	-0.06090400	C	-6.15995700	0.79794500	-0.53701500
C	3.48565300	-2.03858900	-1.55627800	H	-6.43575500	1.72008900	-0.01472100
H	3.75159300	-1.03767200	-1.88565100	H	-6.36683300	0.93527000	-1.60346700
H	3.59140000	-2.83415400	-2.28837300	H	-6.82882400	0.00593500	-0.17449900
C	2.85681200	-1.29769700	0.80381200	C	1.73408400	0.91482600	-0.06843200
H	1.94612800	-1.53557400	1.35544300	C	2.88561500	0.15116700	0.37645100
H	3.67337400	-1.45218500	1.52494300	C	1.95881200	2.25723600	-0.54354100
O	-0.17190500	-0.83916000	1.94209700	C	4.12639500	0.78661600	0.35059400
O	-0.06097300	-1.93145500	-0.35812700	C	3.20702200	2.84014800	-0.55486500
C	-2.05058800	-0.28092700	0.17416900	H	1.07884200	2.79622700	-0.87747900
C	-2.65175700	-0.62896700	-1.03561300	C	4.30758600	2.10071100	-0.09627800
C	-2.75831200	0.41148400	1.15707400	H	4.99345600	0.22341700	0.68608700
C	-3.97754400	-0.26401800	-1.26234300	H	3.33417100	3.85866900	-0.90954000
H	-2.08974800	-1.18427900	-1.77893700	H	5.30146700	2.53919200	-0.09103600
C	-4.08324100	0.76752400	0.91280200				
H	-2.27819400	0.65576300	2.09861000				

TS-C

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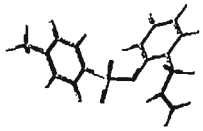
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=383.15

- Thermochemistry -

Zero-point correction= 0.283624 (Hartree/Particle)
Thermal correction to Energy= 0.312508
Thermal correction to Enthalpy= 0.313721
Thermal correction to Gibbs Free Energy= 0.213683
Sum of electronic and zero-point Energies= -1222.270042
Sum of electronic and thermal Energies= -1222.241159
Sum of electronic and thermal Enthalpies= -1222.239945
Sum of electronic and thermal Free Energies= -1222.339984



N	0.95199400	-0.64207400	-0.66760500	H	2.40679200	-2.48492200	0.16930300
S	0.01566000	-1.37529300	0.56928700	C	3.23345800	-1.84955900	-1.66045500
C	2.86317000	-1.64730600	-0.34954300	H	3.81436100	-1.11118000	-2.20780900

H	2.87774200	-2.71387800	-2.21161200	H	-3.68940600	1.69240500	1.54569900
C	3.43465900	-0.51944700	0.48937300	C	-5.47611900	1.07896200	-0.43310600
H	3.30006000	-0.75622500	1.55113300	H	-5.59043200	2.04641800	0.06568200
H	4.51255900	-0.42425800	0.30881500	H	-5.67133800	1.22058000	-1.50182100
O	0.45717300	-0.97262500	1.91593900	H	-6.26053900	0.41479300	-0.04668800
O	-0.05154100	-2.79981900	0.21955700	C	1.44666100	0.65949600	-0.38924500
C	-1.59118800	-0.64195900	0.26957200	C	2.73204700	0.78361700	0.16455800
C	-2.35601400	-1.08684700	-0.81331900	C	0.72155200	1.80557800	-0.74573500
C	-2.06021600	0.35815700	1.12172300	C	3.27646700	2.05051100	0.36940400
C	-3.60477900	-0.51543200	-1.03739400	C	1.26992300	3.06813300	-0.51615000
H	-1.97626900	-1.87312600	-1.45702500	H	-0.25710300	1.69701800	-1.20107200
C	-3.31618200	0.91598700	0.88243200	C	2.54430600	3.19423100	0.04060500
H	-1.45065700	0.67940000	1.95932400	H	4.27725200	2.14499300	0.78460100
C	-4.10548900	0.49115500	-0.19496700	H	0.70459900	3.95471200	-0.79064100
H	-4.20550400	-0.85807100	-1.87654700	H	2.97476300	4.17844000	0.20280400

GS-Li

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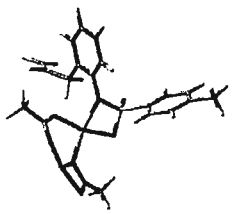
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=373.15

- Thermochemistry -

Zero-point correction= 0.401222 (Hartree/Particle)
Thermal correction to Energy= 0.447933
Thermal correction to Enthalpy= 0.449115
Thermal correction to Gibbs Free Energy= 0.300807
Sum of electronic and zero-point Energies= -1876.001939
Sum of electronic and thermal Energies= -1875.955228
Sum of electronic and thermal Enthalpies= -1875.954046
Sum of electronic and thermal Free Energies= -1876.102354



Cu	-1.10584700	-1.30008400	0.06772200	O	1.23386400	0.33751300	-2.58183100
O	-3.96266400	0.02092700	1.18562200	O	0.26564700	-1.75461800	-1.45016700
C	-2.93867600	0.03695800	1.98599600	C	2.61754500	-0.78979200	-0.65486000
C	-3.10885800	0.85131200	3.24076000	C	2.78207400	-1.88963300	0.19242100
H	-4.00864700	1.46575800	3.19029900	C	3.68840000	0.05779700	-0.94319800
H	-2.22244100	1.47394400	3.38796100	C	4.03276400	-2.13172200	0.75438100
H	-3.18332500	0.17002500	4.09586500	H	1.95152500	-2.56146900	0.38268500
O	-1.86916200	-0.57145400	1.78312200	C	4.93222200	-0.19914700	-0.36791000
N	0.04779000	0.26357300	-0.24767700	H	3.55111400	0.89078000	-1.62397400
S	1.00569200	-0.42587000	-1.35182000	C	5.12451000	-1.28952100	0.49099300
C	-1.82261900	3.87003500	-1.71086800	H	4.16664000	-2.99543500	1.40110000
H	-2.62813800	3.91796700	-0.97612400	H	5.76880800	0.45618700	-0.59709100
C	-1.77398700	4.78282800	-2.68252600	C	6.46812500	-1.54543800	1.13113400
H	-0.98764300	4.77349700	-3.43481600	H	7.28455900	-1.13758300	0.52665800
H	-2.52285700	5.56553300	-2.77135000	H	6.52734200	-1.07431800	2.12139700
C	-0.84669900	2.73578600	-1.54172200	H	6.64858600	-2.61655500	1.27014500
H	-1.37265000	1.77944800	-1.65685600	C	0.30777200	1.51142900	0.38514400
H	-0.10747200	2.75638700	-2.35281100	C	-0.13084100	2.72237400	-0.19900700

C	0.95354200	1.52402600	1.63132000	C	-3.25388300	-2.80818400	-0.54030100
C	0.12499700	3.91532900	0.49037100	O	-2.07955100	-2.94491700	-0.04052300
C	1.18609300	2.72202700	2.30336600	C	-3.93598600	-4.08072600	-0.99867200
H	1.26543900	0.57744500	2.06252400	H	-5.00333300	-3.91048300	-1.14928400
C	0.77407200	3.92401700	1.72528700	H	-3.77151200	-4.88167900	-0.27263400
H	-0.19972300	4.85150900	0.04484200	H	-3.48732200	-4.39903500	-1.94687500
H	1.68872600	2.71617100	3.26689900	O	-3.82739400	-1.69905100	-0.69053400
H	0.95331000	4.86716400	2.23493800	H	-3.83634000	-0.63964300	0.39726500

TS-Li

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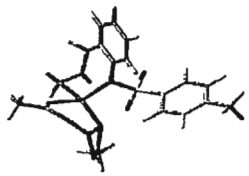
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=373.15

- Thermochemistry -

Zero-point correction= 0.400984 (Hartree/Particle)
Thermal correction to Energy= 0.446337
Thermal correction to Enthalpy= 0.447519
Thermal correction to Gibbs Free Energy= 0.305588
Sum of electronic and zero-point Energies= -1875.979746
Sum of electronic and thermal Energies= -1875.934392
Sum of electronic and thermal Enthalpies= -1875.933211
Sum of electronic and thermal Free Energies= -1876.075142



Cu	-1.65125000	-0.23486700	-0.60204000	H	3.64899400	1.59832400	-0.45992500
O	-3.84453400	-1.27553800	1.01469800	C	4.52673800	-1.69497900	-0.15394400
C	-4.03310700	-1.54050300	-0.20196600	H	3.28896700	-3.34102400	-0.79497400
C	-5.34455900	-2.18479600	-0.61768200	H	5.50459300	0.15827700	0.35704700
H	-5.50508600	-2.10452300	-1.69436800	C	5.67307800	-2.56871500	0.29706700
H	-6.17144000	-1.72302300	-0.07092500	H	5.32617000	-3.56094200	0.60350300
H	-5.32115900	-3.24563800	-0.34075900	H	6.39795000	-2.71338400	-0.51503200
O	-3.18245500	-1.31613800	-1.12997100	H	6.21301600	-2.12024500	1.13759400
N	-0.08545900	1.06687900	-0.45238700	C	0.21299900	1.68812100	0.79505900
S	1.10788400	0.97310300	-1.65799400	C	-0.36318000	2.95155900	0.98702400
C	-1.48294300	2.36024000	-1.17339000	C	0.94748100	1.07985200	1.82015900
H	-1.04353000	2.46608900	-2.16075700	C	-0.18811700	3.61560800	2.20068100
C	-2.66717500	1.59032300	-1.10091600	C	1.13268400	1.76036800	3.02451400
H	-3.33608200	1.70893300	-0.25003800	H	1.36163900	0.08939300	1.66917200
H	-3.11499000	1.22890200	-2.02222500	C	0.56817200	3.02434800	3.21549900
C	-1.15952700	3.47508900	-0.18806700	H	-0.64059900	4.59199400	2.35604900
H	-0.58484500	4.25159200	-0.70791700	H	1.70829800	1.29617500	3.82059800
H	-2.09391400	3.93389500	0.15648100	H	0.70539700	3.54439100	4.15941700
O	1.67737700	2.31196100	-1.87205500	C	-0.73613200	-2.41261200	1.43172000
O	0.42586800	0.26870600	-2.75486600	O	-0.55662100	-1.78274300	0.37966500
C	2.43000900	-0.07388000	-1.05105400	C	0.33787300	-3.30338900	2.00752700
C	2.31600200	-1.46203900	-1.15579300	H	0.03298700	-4.35021500	1.89632800
C	3.57436200	0.51774600	-0.51107200	H	0.45078000	-3.10995000	3.07834200
C	3.36645400	-2.25997300	-0.70569600	H	1.28236800	-3.14167400	1.48687400
H	1.42481100	-1.90466800	-1.58434600	O	-1.83528100	-2.39431900	2.13916600
C	4.61153200	-0.29802600	-0.06289000	H	-2.58670800	-1.86081700	1.67984700

I-1Li

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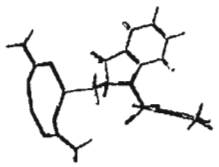
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=373.15

- Thermochemistry -

Zero-point correction= 0.403376 (Hartree/Particle)
Thermal correction to Energy= 0.449242
Thermal correction to Enthalpy= 0.450424
Thermal correction to Gibbs Free Energy= 0.304333
Sum of electronic and zero-point Energies= -1875.989313
Sum of electronic and thermal Energies= -1875.943446
Sum of electronic and thermal Enthalpies= -1875.942264
Sum of electronic and thermal Free Energies= -1876.088356



Cu	-2.77557900	-0.41551800	0.72540600	H	4.93720800	-0.84859200	-1.58757000
O	-4.85344500	-0.47485500	1.20777400	C	5.33564200	-1.84255600	1.66329300
C	-4.70623300	0.65675200	1.80164000	H	3.71434000	-2.02490700	3.07669200
C	-5.90715900	1.33464600	2.41243800	H	6.69992200	-1.56260700	0.01992000
H	-5.64383800	2.32165200	2.79536900	C	6.40004000	-2.25694200	2.65144800
H	-6.29135600	0.71457000	3.23001800	H	6.57340200	-1.47155900	3.39858500
H	-6.70441200	1.41906600	1.66699500	H	6.10725500	-3.16119100	3.19746800
O	-3.55658000	1.16951500	1.88455100	H	7.35377800	-2.45616700	2.15327200
N	1.19924800	0.58583100	-0.55675500	C	1.60139400	1.94659500	-0.56347400
S	2.09145500	-0.61631800	-1.34868100	C	0.48176900	2.78645900	-0.55282700
C	-0.31806900	0.48183500	-0.53057300	C	2.89647800	2.46503800	-0.53161400
H	-0.62987600	-0.06481600	-1.42186500	C	0.64688200	4.16579900	-0.50609100
C	-0.78820100	-0.25755300	0.70491300	C	3.04850700	3.85459200	-0.49799000
H	-0.45987800	-1.30195100	0.71421100	H	3.76496600	1.81698700	-0.54163600
H	-0.53135800	0.26165000	1.63474000	C	1.93925300	4.70329500	-0.48147900
C	-0.78655900	1.96855800	-0.58799600	H	-0.22112800	4.82081700	-0.49406600
H	-1.36556100	2.16458400	-1.49998200	H	4.05047700	4.27495100	-0.48087800
H	-1.44195600	2.19239800	0.26188700	H	2.07853000	5.78015100	-0.45004900
O	2.78113100	-0.07135000	-2.52337000	C	-4.07788100	-1.93297400	-1.54157700
O	1.17196300	-1.75106000	-1.48849400	O	-3.03072700	-1.58990700	-0.97597200
C	3.35505000	-1.04025400	-0.14675600	C	-4.06234300	-2.74940700	-2.80476800
C	2.99794300	-1.37446800	1.16272200	H	-4.72345700	-2.29879700	-3.55096600
C	4.68313100	-1.10860400	-0.56568100	H	-4.44866600	-3.75179700	-2.58808200
C	3.98856300	-1.76889200	2.05596700	H	-3.04460100	-2.82474900	-3.18769200
H	1.96140200	-1.31252100	1.47761800	O	-5.28805500	-1.64149400	-1.11156100
C	5.66363700	-1.50881900	0.34402500	H	-5.24676300	-1.14225700	-0.24173600

GS-E

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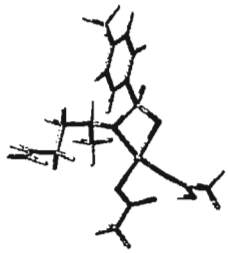
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406350 (Hartree/Particle)
Thermal correction to Energy= 0.458204
Thermal correction to Enthalpy= 0.459481
Thermal correction to Gibbs Free Energy= 0.294872
Sum of electronic and zero-point Energies= -1762.885616
Sum of electronic and thermal Energies= -1762.833762
Sum of electronic and thermal Enthalpies= -1762.832485
Sum of electronic and thermal Free Energies= -1762.997094



O	-2.61155500	0.94646500	0.46925400
C	-3.72241700	0.69243000	-0.12167500
C	-4.80358600	1.75089400	-0.02545800
H	-5.76660300	1.27696900	0.18454200
H	-4.56765000	2.49319700	0.73893000
H	-4.89061600	2.25207300	-0.99665400
O	-3.93464100	-0.35153000	-0.78934300
Cu	-1.29421700	-0.42110900	0.05286200
O	-1.96758900	-1.84690000	1.30639100
C	-2.82382700	-2.73663100	1.15750400
C	-2.78356800	-3.99159900	1.98591400
H	-2.30730700	-4.78198000	1.39340900
H	-2.19215100	-3.82577300	2.88716400
H	-3.79474600	-4.32089900	2.23594900
N	0.16472100	0.62691100	-0.83195600
S	0.95624000	-0.66949600	-1.35606700
C	0.59096400	4.34486200	1.57668800
H	0.90274300	5.29410500	1.13523500
C	0.81033100	4.13651000	2.87596000
H	0.51612300	3.20788200	3.36212600
H	1.28340000	4.88540700	3.50602600
C	0.32918900	1.93133800	-1.51420800
C	-0.05187900	3.36355000	0.63396200
H	-0.97650800	3.80241100	0.23329700
H	-0.35036600	2.46147400	1.17903500
C	0.87934000	2.98859000	-0.53462800
H	1.11949200	3.89327300	-1.11239600
O	0.07840000	-1.74017800	-0.70166300
O	1.20233500	-0.78651900	-2.79872000
H	1.08522700	1.80092600	-2.30050100
C	-0.97226800	2.35148100	-2.20804700
H	-0.84368200	3.31829900	-2.70980600
H	-1.25419600	1.60745000	-2.95977500
H	-1.78945300	2.43998100	-1.48760200
H	1.82833500	2.61682100	-0.12866600
C	2.55657000	-0.77121200	-0.55118800
C	3.64581900	-1.27034400	-1.26677500
C	2.69499200	-0.38411200	0.78529200
C	4.88216700	-1.38428200	-0.63158900
H	3.51906500	-1.55992800	-2.30411900
C	3.93696500	-0.50379400	1.40220500
H	1.84507300	0.01686700	1.32764200
C	5.04921600	-1.00375900	0.70650300
H	5.73121100	-1.77507500	-1.18693900
H	4.04677900	-0.20184300	2.44091600
C	6.39856900	-1.09888900	1.37800600
H	7.03032100	-1.85598600	0.90267500
H	6.93433500	-0.14200400	1.32057100
H	6.30140100	-1.35240400	2.43904400
O	-3.79518400	-2.68630400	0.28848900
H	-3.80441500	-1.78599900	-0.19838900

***cis*-TS-E_{ch}**

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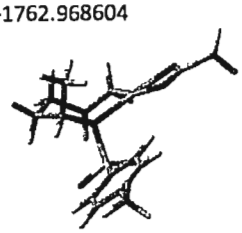
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406492 (Hartree/Particle)
Thermal correction to Energy= 0.456322
Thermal correction to Enthalpy= 0.457598
Thermal correction to Gibbs Free Energy= 0.304075
Sum of electronic and zero-point Energies= -1762.866187
Sum of electronic and thermal Energies= -1762.816358
Sum of electronic and thermal Enthalpies= -1762.815081
Sum of electronic and thermal Free Energies= -1762.968604



O	-0.54327200	1.73132900	0.10161600	H	0.13091400	-3.33245000	2.99211300
C	-0.82978000	2.68506100	0.83788600	O	1.76413900	-2.84689300	-0.92203800
C	0.15566000	3.79849800	1.09860500	O	0.45651100	-1.04543400	-2.17006900
H	0.11564700	4.10426100	2.14748900	H	1.58445400	-1.52868500	1.70554800
H	1.16288600	3.47868000	0.82812000	C	-0.11692900	-0.63618000	2.64743100
H	-0.12094400	4.66801800	0.49077900	H	0.19448800	-0.88601700	3.66840600
O	-1.97675100	2.84433000	1.44628300	H	0.21486900	0.38068600	2.42289700
Cu	-1.52232600	-0.10060500	-0.41381400	H	-1.21219500	-0.64878300	2.61479800
O	-3.01807500	0.75901500	-1.36013100	H	0.80364600	-3.75211700	1.40608100
C	-3.93104500	1.17419800	-0.57260100	C	2.51609400	-0.34477500	-0.63323700
C	-5.23486800	1.63552300	-1.20089000	C	2.38351200	0.99918400	-0.99382300
H	-5.33695600	2.71770700	-1.05965800	C	3.70061100	-0.82331900	-0.06955500
H	-5.26988400	1.40397300	-2.26677500	C	3.44979600	1.86604200	-0.76774000
H	-6.07535200	1.16271300	-0.68316500	H	1.46527700	1.35422300	-1.44504300
N	0.04197200	-1.30897800	0.27088200	C	4.75426400	0.06292600	0.15534700
S	1.17666000	-1.49543000	-0.96521300	H	3.80066900	-1.87900600	0.15851200
C	-1.34916700	-2.71162200	-0.06240900	C	4.64613600	1.41755800	-0.18458400
H	-0.76906100	-3.26676200	-0.79582800	H	3.35816500	2.90887800	-1.06301900
C	-2.47955200	-1.99334400	-0.53648400	H	5.67958500	-0.30871000	0.58840100
H	-3.31143900	-1.82168500	0.14461800	C	5.78303400	2.37771600	0.07311800
H	-2.71755200	-2.01701000	-1.59594700	H	6.72668300	1.84801300	0.23615800
C	0.49312100	-1.62664700	1.65162200	H	5.92106600	3.06832600	-0.76617600
C	-1.30391500	-3.28345900	1.33552100	H	5.58923700	2.98797800	0.96519000
H	-1.56202900	-4.34904600	1.27715700	O	-3.81100800	1.22846200	0.68431400
H	-2.06553600	-2.80151000	1.95958500	H	-2.66237400	2.12592500	1.17128800
C	0.09810500	-3.09349600	1.92288100				

***cis*-I-1E**

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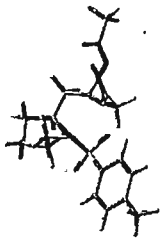
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.407122 (Hartree/Particle)
Thermal correction to Energy= 0.457394
Thermal correction to Enthalpy= 0.458671
Thermal correction to Gibbs Free Energy= 0.301450
Sum of electronic and zero-point Energies= -1762.876555
Sum of electronic and thermal Energies= -1762.826283
Sum of electronic and thermal Enthalpies= -1762.825006
Sum of electronic and thermal Free Energies= -1762.982227



O	-0.75440500	1.67530600	0.21840200	H	0.48613100	-3.08369800	3.27380200
C	-1.18868000	2.62712600	0.89588600	O	2.06219500	-2.79514200	-1.05344100
C	-0.29467200	3.79661500	1.23522500	O	0.50214300	-1.11829400	-2.17464300
H	-0.43374300	4.08634300	2.28040500	H	1.99601000	-1.61158500	1.53385700
H	0.74957600	3.54694000	1.04218900	C	0.50778800	-0.48631500	2.58669800
H	-0.58142100	4.65508300	0.61674600	H	1.03367000	-0.56825100	3.54532100
O	-2.39514400	2.72956800	1.35826400	H	0.76160800	0.47296000	2.12834800
Cu	-1.59322700	-0.12518200	-0.34734300	H	-0.56937200	-0.49168100	2.78721800
O	-3.18373500	0.52816500	-1.37123400	H	1.14287800	-3.79704200	1.78834900
C	-4.18339800	0.87030900	-0.66433700	C	2.52271200	-0.22525700	-0.68455900
C	-5.53086400	0.97266600	-1.35941400	C	2.18640200	1.11270300	-0.90708600
H	-5.87346000	2.01309700	-1.33221300	C	3.81413800	-0.59008300	-0.29653900
H	-5.47169700	0.63201000	-2.39438200	C	3.15842700	2.09070900	-0.70885600
H	-6.26704300	0.37707000	-0.80965400	H	1.18696500	1.38460400	-1.22204700
N	0.23637400	-1.50148300	0.32248000	C	4.77047900	0.40524700	-0.10190100
S	1.33091500	-1.51895500	-1.03057600	H	4.06377600	-1.63846600	-0.17381500
C	-0.80303900	-2.65361300	0.15617100	C	4.45923600	1.75750500	-0.29969200
H	-0.34360300	-3.42080000	-0.47796800	H	2.90587400	3.13275900	-0.89014600
C	-2.05832200	-2.06931400	-0.44373000	H	5.77763200	0.12491500	0.19567700
H	-2.96693000	-2.23843300	0.13895200	C	5.49288100	2.83395700	-0.07006400
H	-2.20820200	-2.27082100	-1.50460600	H	6.50909000	2.42985300	-0.10984100
C	0.91184100	-1.64234400	1.67090200	H	5.41269900	3.63087100	-0.81715700
C	-0.92882700	-3.19853600	1.58340700	H	5.36226300	3.29955700	0.91582700
H	-1.27042700	-4.23811300	1.57242700	O	-4.13797600	1.13203900	0.57430600
H	-1.66911000	-2.61286300	2.14261700	H	-3.05750000	1.96730800	1.02655300
C	0.46957100	-3.02651100	2.18041000				

I-2F

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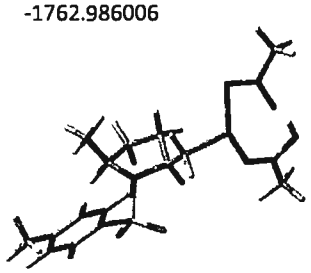
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.408400 (Hartree/Particle)
Thermal correction to Energy= 0.459096
Thermal correction to Enthalpy= 0.460372
Thermal correction to Gibbs Free Energy= 0.297983
Sum of electronic and zero-point Energies= -1762.875589
Sum of electronic and thermal Energies= -1762.824893
Sum of electronic and thermal Enthalpies= -1762.823617
Sum of electronic and thermal Free Energies= -1762.986006



O	-3.08914000	-1.35071700	-0.68122500		H	0.34082200	-1.07298400	3.93888900
C	-4.18400700	-1.90667800	-0.84405400		O	2.69255700	-2.61792900	0.17294800
C	-4.29263000	-3.39308800	-1.05256700		O	1.46427400	-1.26718200	-1.59387400
H	-4.58577600	-3.58699300	-2.09063800		H	2.50478200	-1.40319900	2.29750100
H	-3.33346500	-3.87054700	-0.85185400		C	2.13748200	0.64372100	2.86919400
H	-5.07370600	-3.80805400	-0.40892300		H	2.44636400	0.48159700	3.90916700
O	-5.34239500	-1.28282100	-0.86525000		H	2.98523800	1.06448300	2.31979300
Cu	-2.66882400	0.67992400	-0.36920500		H	1.33165100	1.38611900	2.86376400
O	-3.40463600	2.42312400	0.58861600		H	0.38038700	-2.34255000	2.70043400
C	-4.53494900	2.22919300	0.06640800		C	3.68177300	-0.27489600	-0.50328200
C	-5.70088300	3.13695100	0.37320000		C	3.53690400	1.06341300	-0.88382800
H	-6.54438400	2.54280700	0.74033300		C	4.94487000	-0.83069000	-0.31269300
H	-5.42417500	3.88933900	1.11308600		C	4.67326600	1.84493100	-1.06164300
H	-6.02786900	3.62813600	-0.54971300		H	2.54648000	1.48212200	-1.02971800
N	1.31301600	-0.48620900	0.80355900		C	6.07554000	-0.03150800	-0.49718900
S	2.22960500	-1.31710200	-0.34166000		H	5.03262300	-1.87270400	-0.02495500
C	-0.19216200	-0.52859800	0.61354800		C	5.96004700	1.31180300	-0.87159600
H	-0.45848100	-1.45335300	0.09326600		H	4.56391700	2.88640800	-1.35526000
C	-0.68566100	0.65713400	-0.18662700		H	7.06243200	-0.46253800	-0.34810600
H	-0.35464300	0.62570400	-1.23000600		C	7.18233700	2.17814400	-1.06425800
H	-0.44733300	1.61740000	0.28230800		H	8.10490600	1.60054800	-0.95196200
C	1.68788200	-0.67864200	2.23815400		H	7.19143400	2.63750900	-2.06008700
C	-0.71541500	-0.57990500	2.06353600		H	7.20875100	2.99612800	-0.33319100
H	-1.66690000	-1.11919500	2.11544600		O	-4.69764000	1.25374000	-0.75758500
H	-0.89291500	0.43787100	2.43149300		H	-5.21531100	-0.28831400	-0.77771100
C	0.40429300	-1.25831100	2.86140000					

I-3F/G

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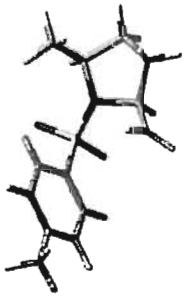
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.290285 (Hartree/Particle)
Thermal correction to Energy= 0.320721
Thermal correction to Enthalpy= 0.321997
Thermal correction to Gibbs Free Energy= 0.217461
Sum of electronic and zero-point Energies= -1109.182967
Sum of electronic and thermal Energies= -1109.152531
Sum of electronic and thermal Enthalpies= -1109.151254
Sum of electronic and thermal Free Energies= -1109.255791



N	1.50935800	0.05735200	-0.08350500	H	1.82040300	-1.84470400	-2.03304200
S	0.48863700	-0.85289800	0.91526500	H	2.41849100	-0.29248400	-2.66184000
C	1.74693000	1.47622000	0.32559000	H	4.31431800	0.41728900	0.61851000
H	1.96518800	1.51868000	1.40187400	C	-1.15461900	-0.40190700	0.35369300
C	0.59565300	2.36350600	0.01170400	C	-1.55477200	-0.72821800	-0.94580600
H	0.08445200	2.26945100	-0.94063000	C	-2.03722000	0.20806500	1.24219700
H	0.33418500	3.18633600	0.66767700	C	-2.84765600	-0.41997500	-1.35443200
C	2.77970300	-0.61000200	-0.53501600	H	-0.86135500	-1.21521900	-1.62349900
C	3.04470800	1.80572600	-0.45351500	C	-3.33315000	0.50677900	0.81631700
H	3.56079700	2.66658600	-0.01859500	H	-1.70800500	0.43992700	2.24911700
H	2.79743400	2.04883900	-1.49330100	C	-3.75719500	0.20297600	-0.48230000
C	3.84054600	0.49892700	-0.36672800	H	-3.16200200	-0.67033400	-2.36506700
H	4.62854900	0.42563000	-1.12321100	H	-4.02441100	0.98267800	1.50735400
O	0.72654100	-2.25776700	0.55854400	C	-5.15646800	0.53261800	-0.94593800
O	0.60569800	-0.41543900	2.31524900	H	-5.75604900	0.96217000	-0.13771100
H	3.00308300	-1.46136500	0.11267700	H	-5.14135200	1.25500500	-1.77180600
C	2.63388100	-1.11588900	-1.97091300	H	-5.67543400	-0.36177800	-1.31141700
H	3.55804900	-1.60910800	-2.29625100				

4

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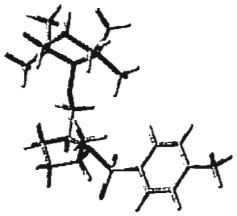
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.562220 (Hartree/Particle)
Thermal correction to Energy= 0.613717
Thermal correction to Enthalpy= 0.614994
Thermal correction to Gibbs Free Energy= 0.466306
Sum of electronic and zero-point Energies= -1592.687734
Sum of electronic and thermal Energies= -1592.636237
Sum of electronic and thermal Enthalpies= -1592.634960
Sum of electronic and thermal Free Energies= -1592.783648



N	0.95585000	-1.34833900	0.06422300	H	5.68789100	4.16188600	-0.14475500
S	2.31756200	-1.42518200	-0.95183900	H	5.14396300	3.97485400	1.52311700
C	-0.23209100	-2.10003200	-0.48089300	H	6.62286000	3.16675900	0.98529500
H	0.10130300	-2.75877000	-1.29047900	C	-2.53767800	1.83735100	-0.30185100
C	-1.27963200	-1.17765800	-1.10523200	C	-2.73274600	2.09118400	1.21293800
H	-0.79325000	-0.50149200	-1.81370500	C	-4.12830900	1.69827400	1.71440800
H	-1.99772300	-1.79234800	-1.66340800	C	-4.44791100	0.24537500	1.34076600
C	1.20413300	-1.75218900	1.48654100	C	-4.28743900	-0.03890800	-0.17196700
C	-0.73052800	-2.95650700	0.70507200	H	-4.17838900	1.82040200	2.80383800
H	-1.13438900	-3.91295300	0.35855400	H	-1.98065500	1.50858700	1.75980700
H	-1.52759700	-2.42895000	1.23514200	H	-2.53109400	3.14878100	1.42901200
C	0.50269500	-3.11750600	1.60234100	H	-3.77026800	-0.42056100	1.89022500
H	0.25133300	-3.37596000	2.63642700	H	-5.46839500	-0.01597200	1.65081000
O	3.13750600	-2.61712100	-0.67186900	H	-4.88791600	2.37458600	1.30094900
O	1.81140400	-1.19869900	-2.31171100	N	-2.94925800	0.43523100	-0.69314400
H	2.28059800	-1.85757600	1.64576700	O	-1.95576200	-0.44538200	-0.08423700
C	0.65850600	-0.68353800	2.43704400	C	-3.31758800	2.86827500	-1.14952100
H	0.82061900	-0.98259400	3.47975700	H	-2.78423500	3.82479500	-1.11958800
H	1.16805100	0.27054800	2.26800400	H	-3.37044700	2.54271700	-2.19295100
H	-0.41264500	-0.52378800	2.27969000	H	-4.33078200	3.06107300	-0.79561400
H	1.16551400	-3.89449900	1.20509200	C	-1.05245300	2.02624400	-0.66308400
C	3.26507000	0.00529000	-0.43285200	H	-0.89592900	1.89183800	-1.73974200
C	4.48883900	-0.17887400	0.20845400	H	-0.75020500	3.04768100	-0.40393400
C	2.79920000	1.28794700	-0.73773100	H	-0.41167400	1.32876800	-0.12295800
C	5.24463700	0.93960000	0.56510600	C	-4.40697400	-1.55487200	-0.41875000
H	4.84400800	-1.18406700	0.40844800	H	-4.32316500	-1.78626600	-1.48641600
C	3.56581000	2.39051300	-0.37511900	H	-3.64998200	-2.12050000	0.12596000
H	1.85754300	1.41445100	-1.26056700	C	-5.42527700	0.61170600	-0.99130400
C	4.79728300	2.23600900	0.28387800	H	-5.18288000	0.59788500	-2.05841200
H	6.20097200	0.79936000	1.06267600	H	-6.34306700	0.03186000	-0.84385800
H	3.20844300	3.38953900	-0.61334800	H	-5.65055800	1.63821400	-0.70221100
C	5.60939200	3.44582400	0.68130500	H	-5.39181300	-1.89505000	-0.07950600

***cis*-TS-E_{bt}**

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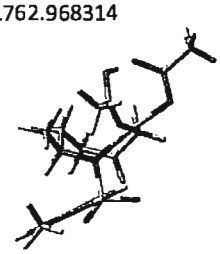
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406722 (Hartree/Particle)
Thermal correction to Energy= 0.456519
Thermal correction to Enthalpy= 0.457795
Thermal correction to Gibbs Free Energy= 0.304462
Sum of electronic and zero-point Energies= -1762.866054
Sum of electronic and thermal Energies= -1762.816257
Sum of electronic and thermal Enthalpies= -1762.814980
Sum of electronic and thermal Free Energies= -1762.968314



O	-3.08518800	0.86321400	-1.29953200	H	-1.86053100	-1.60480300	2.35675600
C	-3.86396600	1.34860900	-0.41419100	H	-0.82353800	-2.76025200	3.20021700
C	-5.18563400	1.92672600	-0.88861200	O	1.65767600	-2.99757400	-0.67778400
H	-5.99341700	1.57393500	-0.24041700	O	0.52351100	-1.26735900	-2.17773600
H	-5.15040900	3.01872600	-0.79708500	H	1.04757100	-2.28444800	1.72932900
H	-5.38842100	1.66037300	-1.92741200	C	0.52524600	-0.31371200	2.45061500
Cu	-1.56538900	-0.07427500	-0.46874900	H	0.74444200	-0.56449500	3.49555300
O	-0.42371300	1.71735900	-0.17538200	H	1.39571200	0.19988900	2.03347700
C	-0.54449000	2.67400700	0.59994200	H	-0.32404700	0.37729200	2.43973900
C	0.51906100	3.73854100	0.70943600	C	2.49237000	-0.51082100	-0.56820900
H	0.54468800	4.15621000	1.71847200	C	2.48212800	0.76620300	-1.13426600
H	1.49039900	3.32401400	0.43502800	C	3.57920700	-0.95116400	0.19125500
H	0.27613400	4.55100300	0.01394100	C	3.57129700	1.60867200	-0.91864100
O	-1.57911400	2.87856800	1.37862600	H	1.64080800	1.08533400	-1.73716900
N	-0.09470700	-1.34068200	0.23546400	C	4.65470500	-0.08985800	0.40321800
S	1.13068300	-1.63761800	-0.88824800	H	3.59083100	-1.96325100	0.58112200
C	-1.51590200	-2.71883300	-0.17958800	C	4.66787700	1.20130200	-0.14300000
H	-0.99332200	-3.21861000	-0.99006400	H	3.57763000	2.59590800	-1.37493700
C	-2.62754600	-1.91626500	-0.54671200	H	5.50482600	-0.43280500	0.98781300
H	-3.41229000	-1.72689000	0.18390100	C	5.82930000	2.13467600	0.10381800
H	-2.92553600	-1.88033100	-1.59095900	H	6.75662300	1.58176300	0.28506300
C	0.19936500	-1.58913300	1.66795100	H	5.99267400	2.80473300	-0.74674100
C	-1.41581300	-3.37813900	1.18044700	H	5.64798300	2.76502700	0.98475000
H	-0.64650700	-4.15718200	1.15052900	O	-3.59249600	1.38185000	0.82043700
H	-2.37188800	-3.85488500	1.42764000	H	-2.33726700	2.21241200	1.18649600
C	-1.03724400	-2.31856200	2.22043400				

***trans*-TS-E_{ch}**

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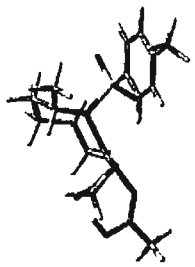
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406896 (Hartree/Particle)
Thermal correction to Energy= 0.456620
Thermal correction to Enthalpy= 0.457897
Thermal correction to Gibbs Free Energy= 0.305228
Sum of electronic and zero-point Energies= -1762.861287
Sum of electronic and thermal Energies= -1762.811563
Sum of electronic and thermal Enthalpies= -1762.810286
Sum of electronic and thermal Free Energies= -1762.962955



O	-2.96700900	-0.87223900	-1.38261000	H	1.84512200	1.53480500	3.29705800
C	-4.05685600	-1.32225700	-1.00057400	H	1.96356400	0.15721200	2.18678500
C	-5.09612000	-1.79450100	-1.98397900	H	2.63057600	1.73782300	1.72392000
H	-4.77138700	-1.58704400	-3.00368600	C	0.17513300	3.15227100	1.75603600
H	-6.05072300	-1.29921800	-1.78014100	H	0.14360100	3.49562500	2.79683500
H	-5.25353000	-2.87094300	-1.85611700	H	-0.32374400	1.12523300	2.26323500
Cu	-1.46877300	0.04600100	-0.30403500	O	2.00398200	2.58710100	-0.95145900
O	-0.80648300	-1.71186900	0.54054000	O	0.55002400	0.87413100	-2.14583500
C	-1.47937600	-1.80733700	1.61219900	H	0.97576400	3.69453600	1.24105100
C	-1.11895800	-2.89818000	2.60395600	C	2.56455800	0.03060400	-0.63557400
H	-1.13649800	-2.49662400	3.62127200	C	3.90372700	0.41740700	-0.71137500
H	-0.14141600	-3.33044600	2.38179000	C	2.21043600	-1.30545800	-0.42763100
H	-1.87761600	-3.68846100	2.55461400	C	4.89969600	-0.54800600	-0.56791700
O	-2.45416300	-1.03546300	1.88334200	H	4.15263200	1.45827500	-0.88575400
N	0.15427800	1.22372800	0.27239400	C	3.22276600	-2.25127900	-0.27891600
S	1.31125900	1.28394100	-0.94971700	H	1.17065200	-1.60387800	-0.35015900
C	-1.17303500	2.65274900	-0.27781200	C	4.57808200	-1.89340200	-0.34670400
H	-0.53319500	3.09142100	-1.03861700	H	5.94327900	-0.24952300	-0.63237500
C	-2.30753600	1.92429300	-0.72643800	H	2.95213300	-3.29123500	-0.11148100
H	-3.18779000	1.90111300	-0.08404700	C	5.65980200	-2.93134300	-0.16276200
H	-2.48786100	1.84836000	-1.79545100	H	6.60734100	-2.60591500	-0.60386500
C	0.44462900	1.64129200	1.67332100	H	5.84334200	-3.12553400	0.90250600
C	-1.16471800	3.37441200	1.04867800	H	5.38039400	-3.88600500	-0.62154900
H	-1.34250900	4.44078000	0.85570200	O	-4.41927300	-1.43842900	0.25295400
H	-1.99091200	3.01175000	1.67277100	H	-3.65363500	-1.20498600	0.89356200
C	1.80779000	1.23770800	2.24256100				

***trans*-TS-E_{bt}**

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opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406102 (Hartree/Particle)
Thermal correction to Energy= 0.456085
Thermal correction to Enthalpy= 0.457361
Thermal correction to Gibbs Free Energy= 0.302698
Sum of electronic and zero-point Energies= -1762.860815
Sum of electronic and thermal Energies= -1762.810833
Sum of electronic and thermal Enthalpies= -1762.809556
Sum of electronic and thermal Free Energies= -1762.964220

O	2.86671400	0.62740900	-1.58339400	H	-1.80200800	-2.02309400	3.25751000
C	3.95472500	0.97333600	-1.01276900	H	-2.62265000	-1.66507300	1.73540000
C	5.11954000	1.33538500	-1.91882000	H	-1.59589200	-3.09432500	1.85248300
H	5.29249900	2.41647400	-1.86252100	C	0.80629500	-1.69309200	2.45519700
H	4.92103100	1.05628900	-2.95499300	H	1.58249300	-0.92049500	2.38768100
H	6.02865000	0.84355300	-1.55971500	H	0.63534700	-1.89280600	3.51863800
Cu	1.47469500	-0.14944600	-0.46835100	H	-0.67139100	-0.16034100	2.05634600
O	0.78281300	1.70055300	0.43625700	O	-1.83935600	-2.74945800	-0.88910000
C	1.29225300	2.47748800	1.25803300	O	-0.46439900	-0.99195500	-2.10370400
C	0.47639800	3.56100100	1.92251900	C	-2.55976300	-0.22300300	-0.64222100
H	0.69933800	4.51947900	1.43927000	C	-3.87276100	-0.69441100	-0.59195900
H	0.75159400	3.65325900	2.97650500	C	-2.28236300	1.14542300	-0.56534400
H	-0.58907500	3.34984000	1.81997200	C	-4.91821700	0.21885500	-0.45488200
O	2.54558600	2.46380200	1.62171300	H	-4.06246100	-1.75979300	-0.66432100
N	-0.11445100	-1.21536000	0.33210000	C	-3.34118000	2.03909700	-0.42313700
S	-1.23261000	-1.40774400	-0.91249300	H	-1.26009200	1.50573000	-0.59200300
C	1.24687200	-2.69285100	0.20660800	C	-4.67212900	1.59531600	-0.37063600
H	0.62166400	-3.35211000	-0.38909100	H	-5.94174800	-0.14566700	-0.41677400
C	2.35736000	-2.08320600	-0.43525000	H	-3.13086200	3.10433600	-0.35890700
H	3.24090800	-1.84292600	0.15367500	C	-5.80832900	2.58289300	-0.25033000
H	2.51310900	-2.25084800	-1.49687100	H	-6.00691800	3.07167000	-1.21315700
C	-0.48104700	-1.20206200	1.76683400	H	-6.73417000	2.09307600	0.06697400
C	1.26874900	-2.95507300	1.70233300	H	-5.57712200	3.37461000	0.47109400
H	0.61107500	-3.79694700	1.94039100	O	4.12302700	1.03936600	0.23553800
H	2.28279700	-3.23286100	2.01050700	H	3.11851700	1.80102800	1.06305900
C	-1.69689500	-2.05249800	2.16678000				

***trans*-I-1E**

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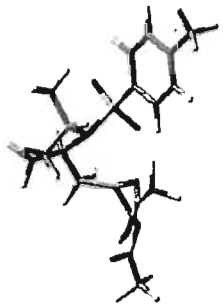
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.406868 (Hartree/Particle)
Thermal correction to Energy= 0.457216
Thermal correction to Enthalpy= 0.458493
Thermal correction to Gibbs Free Energy= 0.301069
Sum of electronic and zero-point Energies= -1762.872368
Sum of electronic and thermal Energies= -1762.822019
Sum of electronic and thermal Enthalpies= -1762.820742
Sum of electronic and thermal Free Energies= -1762.978166



O	3.16514400	0.42532100	-1.48873400		H	-2.24918600	-1.96603700	3.17497900
C	4.22585000	0.74161600	-0.86419200		H	-2.88425900	-1.91398600	1.52756000
C	5.51767800	0.79425300	-1.66257700		H	-1.74395100	-3.18146500	1.98446200
H	5.87538200	1.82932900	-1.70180900		C	0.43114900	-1.51606000	2.59457100
H	5.37325100	0.41830200	-2.67671200		H	1.12134000	-0.66559100	2.56090500
H	6.28586300	0.20733000	-1.14882900		H	0.18004000	-1.70351900	3.64318500
Cu	1.60878900	-0.16889500	-0.40365700		H	-1.11952100	-0.15903600	1.85622000
O	0.87695500	1.62985900	0.35331700		O	-1.99575800	-2.72923900	-1.06469900
C	1.39971100	2.51025200	1.06648200		O	-0.47613700	-0.98347100	-2.11636400
C	0.57198500	3.66544500	1.58082600		C	-2.55323400	-0.17060100	-0.67003600
H	0.74053500	4.53489200	0.93426600		C	-3.89221200	-0.56368800	-0.61253300
H	0.88532900	3.93987000	2.59112900		C	-2.19175400	1.17788200	-0.60265400
H	-0.48955400	3.41263800	1.56204100		C	-4.87864100	0.40982500	-0.46289200
O	2.64491400	2.54779200	1.41593600		H	-4.14834400	-1.61450400	-0.69352800
N	-0.25179900	-1.37886000	0.37757400		C	-3.19448900	2.13243800	-0.44484900
S	-1.31548900	-1.42806900	-0.99404900		H	-1.15052400	1.47682900	-0.64728100
C	0.74222000	-2.57124600	0.38565300		C	-4.54842300	1.76940300	-0.37739100
H	0.22097600	-3.45344300	-0.00393800		H	-5.92171000	0.10697000	-0.41722200
C	1.92825900	-2.15246300	-0.45680700		H	-2.92004400	3.18289900	-0.38379100
H	2.90352600	-2.40933500	-0.03986700		C	-5.62416600	2.82108300	-0.24907200
H	1.85715400	-2.40193500	-1.51616100		H	-5.94141500	3.17726800	-1.23809700
C	-0.81779700	-1.20529600	1.75582400		H	-6.51226700	2.42802500	0.25607200
C	1.04918300	-2.74069600	1.89559300		H	-5.26894300	3.69228600	0.31103200
H	0.59822900	-3.66500800	2.27021100		O	4.28960900	1.01817800	0.37025000
H	2.12644600	-2.80906400	2.06881800		H	3.26520300	1.80524500	0.95453700
C	-1.99295900	-2.12504500	2.12105000					

GS-F

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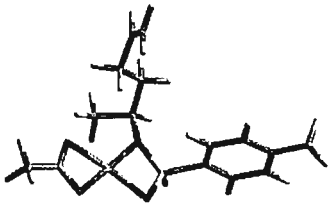
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.343164 (Hartree/Particle)
Thermal correction to Energy= 0.385667
Thermal correction to Enthalpy= 0.386944
Thermal correction to Gibbs Free Energy= 0.247144
Sum of electronic and zero-point Energies= -1533.845378
Sum of electronic and thermal Energies= -1533.802875
Sum of electronic and thermal Enthalpies= -1533.801599
Sum of electronic and thermal Free Energies= -1533.941399



Cu	1.61563000	-1.04282300	-0.24374000	C	-2.27201800	-0.70587100	0.16129800
N	0.33963700	-0.04082000	0.87579800	C	-3.48152400	-1.20402400	0.64811100
S	-0.74370800	-1.23009000	0.93589800	C	-2.24309300	0.16261100	-0.93389500
C	1.01934300	4.24662400	-0.05300800	C	-4.67057600	-0.82846500	0.02415700
H	0.95463400	5.03108300	0.70412900	H	-3.48316300	-1.87101300	1.50317200
C	0.81484900	4.56732800	-1.33158200	C	-3.44048800	0.52770000	-1.54229800
H	0.86998200	3.82142100	-2.12270200	H	-1.29758300	0.55564400	-1.29253300
H	0.59234300	5.58559300	-1.63991500	C	-4.67154000	0.04022700	-1.07534300
C	0.47097900	0.93200100	1.98465700	H	-5.61364300	-1.21745600	0.39987300
C	1.32706300	2.86535600	0.45950700	H	-3.42049700	1.20417100	-2.39318800
H	2.31268400	2.87313800	0.94604400	C	-5.96533600	0.46681800	-1.72674500
H	1.40138100	2.16531000	-0.38072300	H	-6.76474400	-0.25758600	-1.54187600
C	0.26841700	2.36943200	1.46305700	H	-6.30258500	1.43533300	-1.33406100
H	0.24417000	3.04548200	2.33016100	H	-5.85028200	0.57922700	-2.81012700
O	-0.06016700	-2.18691200	-0.04879600	C	3.72382400	-1.00445500	-1.28317800
O	-1.09770700	-1.76064200	2.25817100	C	5.08296200	-1.01376000	-1.92129000
H	-0.33424000	0.73280900	2.70447300	H	5.75874400	-1.61968100	-1.30598500
C	1.80256900	0.72292400	2.71823200	H	5.03016400	-1.46860300	-2.91329500
H	1.92879600	1.46817800	3.51291800	H	5.48407000	0.00014200	-1.98066300
H	1.82519500	-0.27188400	3.17532800	O	3.37415500	-0.07148000	-0.48374000
H	2.65179500	0.80414800	2.03200900	O	2.88504500	-1.94098700	-1.49736900
H	-0.72183600	2.42708400	0.99424400				

cis-TS-F_{bt}

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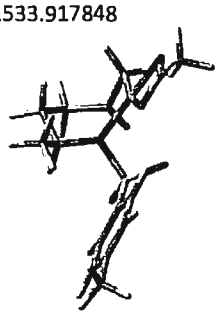
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.343147 (Hartree/Particle)
Thermal correction to Energy= 0.383889
Thermal correction to Enthalpy= 0.385166
Thermal correction to Gibbs Free Energy= 0.254952
Sum of electronic and zero-point Energies= -1533.829654
Sum of electronic and thermal Energies= -1533.788911
Sum of electronic and thermal Enthalpies= -1533.787635
Sum of electronic and thermal Free Energies= -1533.917848



O	-2.87334000	2.29237400	-0.23125900	O	-0.14892600	-0.30258600	-2.16910000
C	-1.85382900	2.99209400	0.10326700	H	0.35436400	-2.55563800	1.19819200
C	-1.96179100	4.49726000	0.10181000	C	0.23193500	-0.81948700	2.48723500
H	-2.92673600	4.80759500	0.51182500	H	0.37611600	-1.37350000	3.42273200
H	-1.14329700	4.94177900	0.67147400	H	1.19721400	-0.40928800	2.18003200
H	-1.91028700	4.85683600	-0.93265700	H	-0.44462000	0.01994400	2.68378700
Cu	-1.84635600	0.58975200	-0.06203900	C	1.98617400	-0.41164900	-0.57462400
N	-0.65028400	-1.03802700	0.14606300	C	2.05302100	0.96675700	-0.34139500
S	0.45073000	-1.15559500	-1.12675800	C	3.10628600	-1.22796800	-0.41183900
C	-2.36620900	-1.93475500	-0.49424000	C	3.26464400	1.51719800	0.06683000
H	-2.00200100	-2.23320700	-1.47335900	H	1.17500100	1.59445800	-0.45223800
C	-3.30407900	-0.86866100	-0.46556400	C	4.31099900	-0.65283600	-0.00631600
H	-3.98764200	-0.78470100	0.37862600	H	3.03025500	-2.29080200	-0.61327200
H	-3.67009200	-0.47229000	-1.41039700	C	4.41059000	0.72280600	0.23752300
C	-0.35323100	-1.74322400	1.41412000	H	3.32130400	2.58642300	0.25634200
C	-2.31073100	-2.99138900	0.58841400	H	5.18733300	-1.28412700	0.11802200
H	-1.70247200	-3.83396100	0.24252000	C	5.72002900	1.34714500	0.65737600
H	-3.32328700	-3.36276000	0.78781900	H	6.15258300	1.94001500	-0.15893100
C	-1.68235200	-2.38578600	1.84872500	H	5.58515500	2.02363700	1.50917800
H	-2.34496300	-1.62026800	2.27475200	H	6.45520400	0.58744200	0.94017500
H	-1.51471000	-3.13835300	2.62716500	O	-0.77083300	2.41000500	0.40565500
O	0.73203400	-2.57371500	-1.40840800				

cis-I-1F

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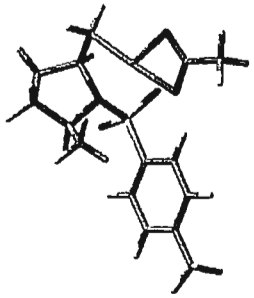
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.344891 (Hartree/Particle)
Thermal correction to Energy= 0.385865
Thermal correction to Enthalpy= 0.387142
Thermal correction to Gibbs Free Energy= 0.256549
Sum of electronic and zero-point Energies= -1533.840158
Sum of electronic and thermal Energies= -1533.799183
Sum of electronic and thermal Enthalpies= -1533.797907
Sum of electronic and thermal Free Energies= -1533.928500



O	-3.05096200	2.35970100	-0.12154300
C	-1.96810700	3.00399900	0.03336500
C	-1.96342400	4.51388900	-0.00683000
H	-2.98044400	4.90789800	0.03154800
H	-1.37227300	4.90661500	0.82596300
H	-1.48451100	4.84500600	-0.93559100
Cu	-1.94847400	0.59797800	-0.00145100
N	-0.67967000	-1.18593700	0.07231100
S	0.49517400	-1.22720400	-1.23134400
C	-1.95315000	-1.99715800	-0.35603000
H	-1.84463200	-2.25694600	-1.41050800
C	-3.10021600	-1.03052400	-0.15671900
H	-3.65248000	-1.15636300	0.77975600
H	-3.77690800	-0.93311800	-1.00737400
C	-0.18597600	-1.73599900	1.39675900
C	-1.89809900	-3.23242700	0.55059800
H	-1.23487900	-3.98657100	0.11125600
H	-2.88943500	-3.67661400	0.68120400
C	-1.30100000	-2.69510500	1.85338000
H	-2.05569400	-2.14179700	2.42571500
H	-0.90269800	-3.47921400	2.50521300
O	0.87456200	-2.62657700	-1.47600900
O	-0.12707600	-0.43002300	-2.29359800
H	0.71735300	-2.32580900	1.19933200
C	0.12903800	-0.63086200	2.40141500
H	0.45470000	-1.07763400	3.34838800
H	0.92009500	0.03418000	2.04662000
H	-0.76162300	-0.02383900	2.60098400
C	1.92763600	-0.37293300	-0.59038500
C	1.90395000	1.01635800	-0.42887300
C	3.07977900	-1.11810000	-0.32818200
C	3.05716800	1.65124900	0.02583200
H	1.00333700	1.58950100	-0.62222700
C	4.22274800	-0.45762600	0.11968400
H	3.07680400	-2.19098600	-0.48615700
C	4.23066800	0.93189000	0.30332200
H	3.04363500	2.72915900	0.16598400
H	5.12294000	-1.03115100	0.32530500
C	5.47809200	1.64676300	0.76425400
H	5.99232600	2.12034200	-0.08232300
H	5.24181600	2.43934600	1.48253600
H	6.18593100	0.95781200	1.23540300
O	-0.87369300	2.37004300	0.20700600

I-2F

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opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.344974 (Hartree/Particle)
Thermal correction to Energy= 0.386131
Thermal correction to Enthalpy= 0.387407
Thermal correction to Gibbs Free Energy= 0.251472
Sum of electronic and zero-point Energies= -1533.823756
Sum of electronic and thermal Energies= -1533.782600
Sum of electronic and thermal Enthalpies= -1533.781323
Sum of electronic and thermal Free Energies= -1533.917258

O	-4.61042600	0.11348400	-0.75562700
C	-5.45209000	-0.64197400	-0.16537300
C	-6.93156800	-0.42469800	-0.35056400
H	-7.12869400	0.53918700	-0.82259000
H	-7.33173800	-1.22487200	-0.98361800
H	-7.43576100	-0.48733600	0.61791700
Cu	-3.13548300	-1.05969600	0.14698200
N	0.57123400	1.04425200	0.00686300
S	1.64691300	0.74106100	1.27176000
C	-0.89564300	0.79836400	0.28879700
H	-1.05744800	0.80799200	1.36848100
C	-1.30049500	-0.55922700	-0.26724700
H	-0.74092000	-1.37358800	0.21512500
H	-1.19612600	-0.61890500	-1.35657600
C	0.77365300	2.28131600	-0.80640200
C	-1.58516200	2.00458400	-0.38628700
H	-1.71711600	2.80784700	0.34858700
H	-2.57205700	1.74331700	-0.77697300
C	-0.59894400	2.45130700	-1.47014300
H	-0.66734300	1.80070900	-2.35144100
H	-0.75929600	3.48163900	-1.80342800
O	2.20496600	2.00119700	1.78717600
O	0.96060800	-0.18830400	2.18024700
H	0.95799500	3.12699300	-0.12953100
C	1.92975400	2.17175100	-1.79829800
H	1.95349600	3.06673800	-2.43128200
H	2.89687400	2.09655600	-1.29336700
H	1.80641900	1.29330300	-2.44105200
C	2.99752000	-0.14625100	0.48834600
C	2.74083400	-1.29454800	-0.26666100
C	4.30422100	0.28300500	0.71256500
C	3.80755300	-2.00438500	-0.80749500
H	1.71901000	-1.61725200	-0.43708000
C	5.36353100	-0.44299600	0.16381000
H	4.48103600	1.17452300	1.30443600
C	5.13528000	-1.59204000	-0.60173600
H	3.61003800	-2.89466500	-1.40019400
H	6.38342200	-0.10801400	0.33528400
C	6.28045300	-2.37595200	-1.19797900
H	6.28482500	-3.41090300	-0.83438200
H	6.20555300	-2.42010900	-2.29159600
H	7.24663600	-1.92846600	-0.94621300
O	-5.02670100	-1.59385100	0.56805800

***cis*-TS-F_{ch}**

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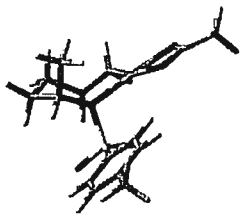
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.343301 (Hartree/Particle)
Thermal correction to Energy= 0.383902
Thermal correction to Enthalpy= 0.385179
Thermal correction to Gibbs Free Energy= 0.255946
Sum of electronic and zero-point Energies= -1533.830087
Sum of electronic and thermal Energies= -1533.789486
Sum of electronic and thermal Enthalpies= -1533.788210
Sum of electronic and thermal Free Energies= -1533.917442



Cu	-1.83685600	0.59616400	-0.09757800	H	0.84805900	-1.91373200	1.41830900
O	-2.87402500	2.29363100	-0.30036400	C	-0.60983600	-0.92328200	2.63667400
C	-1.89104300	2.99208100	0.12940500	H	-0.31548100	-1.44801900	3.55306500
C	-2.00983600	4.49624100	0.15526900	H	-0.10345000	0.04634900	2.61076100
H	-1.80623900	4.88535000	-0.84953600	H	-1.68902300	-0.73702600	2.68796200
H	-3.02581900	4.79316900	0.42788500	H	-0.41509000	-3.76016700	0.62406500
H	-1.28480500	4.92605700	0.84960800	C	1.99839500	-0.35059900	-0.54901000
N	-0.60088200	-1.01459800	0.17021200	C	2.03370300	1.00432600	-0.20053000
S	0.46953200	-1.08946500	-1.12995600	C	3.14528200	-1.14368000	-0.48730300
C	-2.30150200	-1.93777400	-0.40996000	C	3.24179700	1.55416400	0.21955400
H	-1.86499200	-2.38810200	-1.29853200	H	1.13779900	1.61587600	-0.23800400
C	-3.23739500	-0.88512100	-0.60101300	C	4.34512300	-0.56916800	-0.06703400
H	-4.00924400	-0.73036200	0.15207100	H	3.09169100	-2.18801300	-0.77478700
H	-3.49386500	-0.58379400	-1.61415400	C	4.41385400	0.78361200	0.28943100
C	-0.23725800	-1.75306500	1.40399600	H	3.27472500	2.60484600	0.49775400
C	-2.36666900	-2.84655300	0.79559700	H	5.24151500	-1.18252200	-0.01942200
H	-2.85279700	-3.78219000	0.48889700	C	5.71935800	1.40992700	0.71852900
H	-3.00096400	-2.39396800	1.56672000	H	6.46235700	0.65061100	0.98160400
C	-0.95459000	-3.11761100	1.32772400	H	6.14415700	2.02256000	-0.08745200
H	-0.97532400	-3.62257900	2.30037000	H	5.58236300	2.06738500	1.58437800
O	0.76802900	-2.48910400	-1.48150400	O	-0.82778900	2.41111000	0.49988800
O	-0.15613900	-0.20536900	-2.13201400				

***trans*-TS-F_{ch}**

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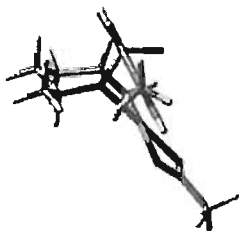
opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.343602 (Hartree/Particle)
Thermal correction to Energy= 0.384108
Thermal correction to Enthalpy= 0.385385
Thermal correction to Gibbs Free Energy= 0.255648
Sum of electronic and zero-point Energies= -1533.824574
Sum of electronic and thermal Energies= -1533.784067
Sum of electronic and thermal Enthalpies= -1533.782790
Sum of electronic and thermal Free Energies= -1533.912527



Cu	1.86526000	0.69658400	-0.05576200	C	-1.92667100	-0.36230100	-0.50368100
N	0.73317300	-0.99750400	0.24505400	C	-3.10843500	-1.09987900	-0.59420100
S	-0.39614800	-1.15671600	-1.01056500	C	-1.94027500	0.98113000	-0.11661600
C	2.39832700	-1.80846300	-0.47333300	C	-4.31872900	-0.48427800	-0.27756100
H	1.94415400	-2.24435900	-1.35956400	H	-3.07295600	-2.13559500	-0.91353800
C	3.27666100	-0.70082200	-0.67885500	C	-3.16046800	1.57140900	0.20530300
H	4.09809600	-0.55652700	0.02214000	H	-1.02456100	1.55952700	-0.04826700
H	3.45918300	-0.36290400	-1.69674900	C	-4.36500300	0.85462600	0.13248100
C	0.58645100	-1.74055400	1.53290800	H	-5.24138000	-1.05447800	-0.35291000
C	2.61440200	-2.78073200	0.66546800	H	-3.17515500	2.61367800	0.51471600
H	3.08766400	-3.68377800	0.25899700	C	-5.67403000	1.50834700	0.50641400
H	3.31086800	-2.34671600	1.39403500	H	-6.52673000	0.97577900	0.07355000
C	-0.82571600	-1.84840500	2.11283800	H	-5.81155400	1.51924000	1.59588000
H	-0.75922900	-2.32701800	3.09670400	H	-5.71294800	2.54878500	0.16601700
H	-1.28566700	-0.86533800	2.24244500	C	1.83050700	3.08432700	0.26127700
H	-1.47717400	-2.46255000	1.48513900	O	2.80611300	2.45714000	-0.27669600
C	1.27507000	-3.09915500	1.33552200	O	0.82753400	2.43409800	0.68539700
H	1.41145600	-3.62152100	2.28975000	C	1.87994700	4.58992300	0.35446400
H	1.18562500	-1.15480200	2.24283900	H	1.61267200	5.01550700	-0.62011600
O	-0.70130600	-2.57744600	-1.25730000	H	1.17101000	4.95171000	1.10198400
O	0.20720700	-0.34673100	-2.08599800	H	2.89343300	4.92200600	0.59443900
H	0.65821200	-3.72910700	0.68548100				

***trans*-TS-F_{bt}**

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opt=(calcfc,ts,noeigen) freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.343591 (Hartree/Particle)
Thermal correction to Energy= 0.384078
Thermal correction to Enthalpy= 0.385354
Thermal correction to Gibbs Free Energy= 0.256644
Sum of electronic and zero-point Energies= -1533.823024
Sum of electronic and thermal Energies= -1533.782537
Sum of electronic and thermal Enthalpies= -1533.781260
Sum of electronic and thermal Free Energies= -1533.909971

Cu	1.86197700	0.57666800	-0.11438700	H	-0.35431500	-3.62318600	0.77670600
O	0.93657600	2.35412400	0.67998000	C	1.68507400	-2.05934000	2.00883100
C	1.96573000	2.95360500	0.24440400	H	2.25805000	-1.16629600	2.28950700
C	2.09160400	4.45450100	0.33805300	H	1.59350400	-2.68379700	2.90399800
H	1.80057800	4.89499800	-0.62305600	H	-0.11688200	-0.86227100	2.12380800
H	3.12897200	4.73792000	0.53366500	O	-0.78274900	-2.33419900	-1.62306800
H	1.43312600	4.84691700	1.11582200	O	0.20523900	-0.03212100	-2.04739700
O	2.90103600	2.27898700	-0.30861500	C	-1.97984800	-0.24786400	-0.52564900
N	0.61705600	-1.03751500	0.16308800	C	-3.16910500	-0.96887200	-0.65406500
S	-0.45849500	-0.98543500	-1.13123500	C	-1.96996300	1.04322400	0.01238300
C	2.32353900	-1.97468300	-0.40503200	C	-4.36332300	-0.38925600	-0.22779000
H	1.88255000	-2.46253800	-1.26983200	H	-3.14977700	-1.96372000	-1.08581700
C	3.23487900	-0.91033400	-0.64164900	C	-3.17493700	1.59809700	0.43840000
H	4.03113800	-0.73341300	0.08047700	H	-1.04575200	1.60532600	0.10743600
H	3.45524100	-0.62720000	-1.66831600	C	-4.38652500	0.89914100	0.32336900
C	0.30006600	-1.64497900	1.47632900	H	-5.29120700	-0.94725300	-0.32692700
C	2.40718700	-2.79851300	0.86642500	H	-3.17253800	2.59798400	0.86566500
H	1.94747700	-3.77848000	0.70529700	C	-5.68637500	1.53338000	0.75781800
H	3.45912600	-2.96634800	1.12373600	H	-6.44510400	0.77838800	0.98739700
C	-0.67808700	-2.82993600	1.45500300	H	-5.54941600	2.16113300	1.64480500
H	-0.75331100	-3.24065300	2.46847500	H	-6.09269100	2.17597600	-0.03454700
H	-1.67989400	-2.52067200	1.14889500				

***trans*-I-1F**

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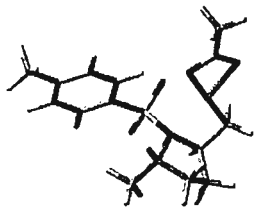
opt=calcfc freq=noraman ub3lyp/genecp gfinput temperature=403.15

- Thermochemistry -

Zero-point correction= 0.345310 (Hartree/Particle)
Thermal correction to Energy= 0.386144
Thermal correction to Enthalpy= 0.387420
Thermal correction to Gibbs Free Energy= 0.257223
Sum of electronic and zero-point Energies= -1533.833538
Sum of electronic and thermal Energies= -1533.792703
Sum of electronic and thermal Enthalpies= -1533.791427
Sum of electronic and thermal Free Energies= -1533.921624



Cu	1.97253900	0.51148900	-0.15121300	H	-0.51899300	-3.65739300	1.07100400
O	1.12535500	2.25916800	0.58272600	C	1.42434400	-1.93466600	2.18328500
C	2.17340600	2.88426100	0.20031700	H	1.97343300	-1.01426700	2.41537600
C	2.25478400	4.38245300	0.37567200	H	1.26780300	-2.47712700	3.12064900
H	1.52990300	4.86181400	-0.29216300	H	-0.36405600	-0.69577200	1.92907700
H	3.25612300	4.74850000	0.14284600	O	-0.98617000	-2.44435500	-1.60087800
H	1.98265900	4.65072900	1.40120500	O	0.17682200	-0.26124500	-2.17987000
O	3.12879100	2.24488000	-0.33422600	C	-1.92880400	-0.20452900	-0.54179100
N	0.59000200	-1.22192900	0.12532200	C	-3.17995700	-0.82598800	-0.57564800
S	-0.52985600	-1.10514500	-1.20572800	C	-1.78378700	1.11465200	-0.10034700
C	1.83012500	-2.10844000	-0.23303400	C	-4.29892400	-0.11847600	-0.14089400
H	1.50877400	-2.86196600	-0.95935700	H	-3.26681900	-1.84262300	-0.94327200
C	2.87911800	-1.15202800	-0.76537400	C	-2.91688400	1.79615700	0.33974300
H	3.87476700	-1.27340700	-0.33417700	H	-0.81529100	1.60538600	-0.07947800
H	2.91583800	-1.07488000	-1.85369800	C	-4.18679000	1.19949200	0.32358400
C	0.09286800	-1.59049300	1.49712900	H	-5.27406700	-0.59829100	-0.16548900
C	2.17618800	-2.75978100	1.12570800	H	-2.80902200	2.81668600	0.69838400
H	1.83977100	-3.80126700	1.14553200	C	-5.40645900	1.97053000	0.76801500
H	3.25665400	-2.76209800	1.29235800	H	-6.20271400	1.30166300	1.10985900
C	-0.90221000	-2.75910200	1.56281400	H	-5.16755900	2.66340700	1.58158000
H	-1.08984800	-2.99512400	2.61665700	H	-5.81282200	2.56795700	-0.05883600
H	-1.86096900	-2.51113600	1.10444100				

Section B:

(*R*,*R*)-Hydrobenzoin 8

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

Zero-point correction= 0.247770 (Hartree/Particle)
Thermal correction to Energy= 0.265083
Thermal correction to Enthalpy= 0.266154
Thermal correction to Gibbs Free Energy= 0.198016
Sum of electronic and zero-point Energies= -692.121518
Sum of electronic and thermal Energies= -692.104205
Sum of electronic and thermal Enthalpies= -692.103134
Sum of electronic and thermal Free Energies= -692.171273

C	-4.64063100	0.41374900	-0.23889200	C	2.77987000	-1.00667300	-0.33698800
C	-3.79962300	1.52952900	-0.22084500	C	2.41537800	1.36744200	-0.11682800
C	-2.44358700	1.37750200	0.07143700	C	4.12822100	-0.82780400	-0.01203900
C	-1.90676000	0.11205700	0.34469300	H	2.40771500	-1.99740700	-0.57972900
C	-2.75578500	-1.00112800	0.32595000	C	3.76044800	1.54846800	0.20478400
C	-4.11437300	-0.84970100	0.03764900	H	1.75201500	2.22889200	-0.16469100
H	-5.69806100	0.52935400	-0.46210400	C	4.62218800	0.44843200	0.26092200
H	-4.19956200	2.51907200	-0.42688200	H	4.79249200	-1.68775800	0.02033000
H	-1.79559500	2.25142000	0.09266300	H	4.13773500	2.54779600	0.40663300
H	-2.35723600	-1.98432200	0.55271900	H	5.67101500	0.58792800	0.50944300
H	-4.76231300	-1.72257500	0.03065300	O	-0.19231400	-1.21835800	1.36289600
C	-0.42195800	-0.01564500	0.61877100	H	0.74347800	-1.21272400	1.63273100
H	-0.09138700	0.85802600	1.19538500	O	0.13777300	-1.31166800	-1.35525800
C	0.42251400	-0.08931600	-0.69340100	H	0.01178400	-1.96504400	-0.64169200
H	0.09919600	0.71901200	-1.35859500				
C	1.90827400	0.08784500	-0.38987300				

Tetralithiated intermediate 12

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

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mp2/6-31g(d)//B3LYP/6-31G(d)

MP2=-717.8595732

C	-0.46712	0.38865	0.14952	H	1.0325	4.53049	1.77718
H	-0.66284	0.11543	1.1974	H	3.21198	2.84568	-1.51047
C	-1.86886	0.76322	-0.50751	H	2.87726	4.66347	0.10933
H	-2.09219	1.80348	-0.22749	C	-3.00833	-0.14614	0.02432
C	0.51375	1.58917	0.12833	C	-3.50966	-1.19743	-0.79545
C	0.32666	2.62581	1.05936	C	-3.49982	0.08589	1.32117
C	1.56213	1.61694	-0.83427	C	-4.51736	-1.99693	-0.2126
C	1.17417	3.73064	1.05354	C	-4.49594	-0.73206	1.84731
H	-0.47554	2.56648	1.79597	H	-3.1088	0.91113	1.9172
C	2.3894	2.76081	-0.79773	C	-5.00628	-1.78438	1.07833
C	2.21153	3.80199	0.11667	H	-4.94414	-2.81937	-0.78935

H	-4.87829	-0.54954	2.84926	Li	-1.47827	-1.33807	-1.35337
H	-5.78638	-2.42506	1.48596	Li	0.10819	0.71184	-2.04731
O	-1.73818	0.64583	-1.92702	Li	-3.33417	0.00366	-2.44115
O	0.07401	-0.72462	-0.56479	Li	1.85597	-0.40916	-0.5877

Trilithiated intermediate 14

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

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mp2/6-31g(d)//B3LYP/6-31G(d)

MP2=-710.9536577

C	-0.46132	-0.23646	-0.63417	C	2.76543	-0.90126	0.18711
H	-0.10569	0.46899	-1.4075	C	2.34281	1.53218	0.05554
C	0.40517	0.02771	0.67605	C	4.09513	-0.60189	-0.19227
H	0.05853	0.97873	1.11238	C	3.66549	1.77174	-0.31753
C	-1.94121	0.10307	-0.38012	H	1.65645	2.37259	0.16332
C	-2.33114	1.38957	0.03233	C	4.55169	0.69741	-0.44393
C	-2.94462	-0.8614	-0.55407	H	4.81693	-1.41583	-0.29512
C	-3.66792	1.68937	0.28939	H	4.00505	2.78922	-0.50057
H	-1.58001	2.16757	0.14699	H	5.58752	0.87508	-0.72887
C	-4.28879	-0.56624	-0.29147	O	0.20155	-1.02911	1.59496
H	-2.67182	-1.84074	-0.94146	O	-0.29709	-1.57157	-1.04358
C	-4.65508	0.70832	0.13765	Li	1.44527	-2.02506	-1.01757
H	-3.94374	2.6922	0.60696	Li	-0.89207	-2.12664	0.63539
H	-5.04706	-1.3321	-0.43796	Li	1.82248	-1.76127	1.83276
H	-5.69682	0.94333	0.34008				
C	1.89068	0.22209	0.29863				

Dilithiated intermediate 13

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

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mp2/6-31g(d)//B3LYP/6-31G(d)

MP2=-704.0490871

C	-0.45839	-0.2701	-0.66539	C	1.90934	0.12426	0.31936
H	-0.07895	0.50505	-1.35287	C	2.97955	-0.70616	0.68728
C	0.45839	-0.2701	0.66539	C	2.20826	1.32004	-0.35856
H	0.07895	0.50505	1.35287	C	4.30185	-0.37329	0.36346
C	-1.90934	0.12426	-0.31936	H	2.77029	-1.60085	1.26983
C	-2.20826	1.32003	0.35856	C	3.52273	1.65717	-0.67722
C	-2.97955	-0.70616	-0.68728	H	1.40528	2.00005	-0.63272
C	-3.52273	1.65717	0.67722	C	4.5777	0.80659	-0.32515
H	-1.40528	2.00005	0.63272	H	5.11256	-1.03197	0.66618
C	-4.30185	-0.37329	-0.36346	H	3.72743	2.58708	-1.20245
H	-2.77029	-1.60085	-1.26983	H	5.60142	1.07081	-0.57711
C	-4.5777	0.80659	0.32515	O	0.38405	-1.54565	1.23653
H	-3.72743	2.58708	1.20245	O	-0.38405	-1.54565	-1.23652
H	-5.11256	-1.03197	-0.66618	Li	1.14603	-2.17199	-0.40348
H	-5.60142	1.07081	0.57711	Li	-1.14603	-2.17199	0.40348

TS-3

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

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mp2/6-31g(d)//B3LYP/6-31G(d)

MP2=-869.1152194

C	-1.55511	-0.04113	-0.68921	H	3.53379	2.11703	-0.0613
H	-1.59489	0.76581	-1.44246	H	0.33176	4.90583	-0.68926
C	-0.87536	0.57335	0.63126	H	2.76791	4.38076	-0.68029
H	-1.65738	1.06588	1.22798	O	-0.30009	-0.50513	1.35435
C	-3.01545	-0.45055	-0.40281	O	-0.78667	-1.12411	-1.12451
C	-3.9519	0.47151	0.09823	Li	0.86249	-0.82479	-0.36194
C	-3.45272	-1.76099	-0.64991	Li	-1.16228	-1.94513	0.54561
C	-5.26525	0.0897	0.36672	C	2.83905	-1.31625	0.71321
H	-3.65262	1.50258	0.27145	H	2.37002	-2.23794	0.31108
C	-4.77009	-2.15099	-0.37294	H	3.01477	-1.55278	1.78308
H	-2.76371	-2.46739	-1.10879	C	4.1967	-1.10701	0.02498
C	-5.67942	-1.22869	0.14129	H	4.70058	-0.23734	0.47579
H	-5.97079	0.82179	0.75221	H	4.03174	-0.83483	-1.03095
H	-5.0838	-3.17162	-0.57934	C	5.16146	-2.30373	0.06875
H	-6.70346	-1.52471	0.3534	H	4.67192	-3.17492	-0.39152
C	0.17815	1.62955	0.27373	H	5.34636	-2.57732	1.11816
C	1.55898	1.30867	0.29302	C	6.49728	-2.03995	-0.63389
C	-0.24853	2.92259	-0.07967	H	7.02789	-1.19474	-0.17629
C	2.4639	2.32951	-0.06302	H	7.16069	-2.91237	-0.58402
H	2.18831	0.01526	0.49895	H	6.34744	-1.79925	-1.69453
C	0.67502	3.90855	-0.42316	Li	1.34668	-0.13098	2.01786
H	-1.31141	3.16246	-0.07703				
C	2.04299	3.61327	-0.41651				

ss

TS-4

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opt=calcfc freq=noraman b3lyp/6-31g(d) scrf=(iefpcm,solvent=diethylether,smd) temperature=338.15

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mp2/6-31g(d)//B3LYP/6-31G(d)

MP2=-876.0265214

C	-0.68197	0.86703	0.64193	H	3.68809	2.50382	-0.04662
H	-1.512	1.36793	1.16474	H	2.87069	4.68711	-0.8732
C	-1.29531	0.13019	-0.62937	C	-2.70709	-0.43313	-0.32929
H	-1.3898	0.87921	-1.43081	C	-2.86327	-1.8228	-0.05771
C	0.34015	1.93623	0.23104	C	-3.79728	0.45646	-0.32468
C	-0.11634	3.18349	-0.23123	C	-4.18542	-2.23703	0.22804
C	1.7282	1.66399	0.30681	C	-5.08031	-0.00626	-0.03759
C	0.78719	4.168	-0.6307	H	-3.64567	1.51112	-0.55611
H	-1.1853	3.3907	-0.26972	C	-5.27762	-1.3633	0.24467
C	2.61209	2.68181	-0.10008	H	-4.38098	-3.28995	0.4437
H	2.429	0.48807	0.78963	H	-5.92232	0.68277	-0.04027
C	2.16296	3.91921	-0.56723	H	-6.27778	-1.73192	0.46691
H	0.42105	5.13022	-0.98181	O	-0.39959	-0.9077	-1.01038

O	-0.08147	-0.11803	1.47112
Li	-0.94498	-1.6523	0.85019
Li	1.16782	-0.52366	-0.08803
Li	-1.45798	-2.28258	-1.55743
C	3.24022	-1.72224	0.08429
H	3.19757	-1.19679	-0.89091
H	2.34709	-2.37562	0.11759
C	4.47126	-2.64569	0.04497
H	4.53312	-3.19397	0.99555
H	5.37379	-2.02091	-0.0088
C	4.46032	-3.63601	-1.12345
H	4.42304	-3.11211	-2.08759
H	5.35793	-4.26655	-1.12441
H	3.589	-4.30259	-1.07462
C	3.19603	-0.69647	1.23261
H	4.17813	-0.20289	1.311
H	3.05596	-1.23424	2.19012
Li	1.48016	0.4024	2.23572

Bisbenzoxaborol 10

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.245177 (Hartree/Particle)
Thermal correction to Energy= 0.260722
Thermal correction to Enthalpy= 0.261666
Thermal correction to Gibbs Free Energy= 0.202068
Sum of electronic and zero-point Energies= -891.286832
Sum of electronic and thermal Energies= -891.271287
Sum of electronic and thermal Enthalpies= -891.270343
Sum of electronic and thermal Free Energies= -891.329940

C	-0.48467500	4.07366600	-1.45618900
C	-0.34434100	2.70622100	-1.70540600
C	0.34434100	1.93039600	-0.77549700
C	0.89428700	2.49252400	0.38709500
C	0.74539700	3.86295100	0.62268300
C	0.05567300	4.65073000	-0.29996700
H	-1.01890900	4.69743600	-2.16823600
H	1.16167100	4.32472800	1.51659700
H	-0.06436300	5.71660800	-0.12499700
C	0.63176800	0.44154900	-0.81646800
C	-0.63176800	-0.44154900	-0.81646800
H	-1.22254600	-0.17227600	-1.70397500
C	-0.34434100	-1.93039600	-0.77549700
C	0.34434100	-2.70622100	-1.70540600
C	-0.89428700	-2.49252400	0.38709500
C	0.48467500	-4.07366600	-1.45618900
C	-0.74539700	-3.86295100	0.62268300
C	-0.05567300	-4.65073000	-0.29996700
H	1.01890900	-4.69743600	-2.16823600
H	-1.16167100	-4.32472800	1.51659700
H	0.06436300	-5.71660800	-0.12499700
O	-1.41588600	-0.15836000	0.34479300
O	1.41588600	0.15836000	0.34479300
H	1.22254600	0.17227600	-1.70397500
H	-0.76791200	2.26944400	-2.60715400
H	0.76791200	-2.26944400	-2.60715400
B	-1.57723600	-1.29107900	1.11462100
B	1.57723600	1.29107900	1.11462100
O	2.26896600	1.20204500	2.28477500
O	-2.26896600	-1.20204500	2.28477500
H	2.31306200	2.05292000	2.74060800
H	-2.31306200	-2.05292000	2.74060800

Bisbenzoxaborol 6-membered isomer 17

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.246423 (Hartree/Particle)
Thermal correction to Energy= 0.261616
Thermal correction to Enthalpy= 0.262560
Thermal correction to Gibbs Free Energy= 0.204627
Sum of electronic and zero-point Energies= -891.300906
Sum of electronic and thermal Energies= -891.285714
Sum of electronic and thermal Enthalpies= -891.284770

Sum of electronic and thermal Free Energies= -891.342702

C	1.09112200	4.15743000	-1.07998800	C	0.85134500	-3.74747200	0.29778700
C	1.29969300	2.78242200	-1.19802400	C	-0.01516100	-4.64150200	-0.33074500
C	0.42975400	1.88862500	-0.57034000	H	-1.76675600	-4.85140300	-1.57347300
C	-0.65969300	2.36279700	0.18484200	H	1.68892700	-4.12098000	0.88100200
C	-0.85134500	3.74747200	0.29778700	H	0.14483300	-5.71277100	-0.24002500
C	0.01516100	4.64150200	-0.33074500	O	-1.51234300	-0.01558600	0.45194200
H	1.76675600	4.85140300	-1.57347300	O	1.51234300	0.01558600	0.45194200
H	-1.68892700	4.12098000	0.88100200	H	1.18624400	0.14646200	-1.57955600
H	-0.14483300	5.71277100	-0.24002500	H	2.14061000	2.40605100	-1.77646100
C	0.65969300	0.39349500	-0.64743100	H	-2.14061000	-2.40605100	-1.77646100
C	-0.65969300	-0.39349500	-0.64743100	B	1.58893600	-1.29888900	0.84124500
H	-1.18624400	-0.14646200	-1.57955600	B	-1.58893600	1.29888900	0.84124500
C	-0.42975400	-1.88862500	-0.57034000	O	-2.49385500	1.64457300	1.80469800
C	-1.29969300	-2.78242200	-1.19802400	O	2.49385500	-1.64457300	1.80469800
C	0.65969300	-2.36279700	0.18484200	H	2.99743900	-0.86708300	2.09255300
C	-1.09112200	-4.15743000	-1.07998800	H	-2.99743900	0.86708300	2.09255300

Bisboronic ester 20

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.301974 (Hartree/Particle)
Thermal correction to Energy= 0.321277
Thermal correction to Enthalpy= 0.322221
Thermal correction to Gibbs Free Energy= 0.251589
Sum of electronic and zero-point Energies= -969.845673
Sum of electronic and thermal Energies= -969.826370
Sum of electronic and thermal Enthalpies= -969.825426
Sum of electronic and thermal Free Energies= -969.896058

C	-3.96159700	-1.77152500	1.06807200	H	4.43947600	1.21549700	0.51082600
C	-2.62894500	-2.01991700	0.72956500	H	5.64781800	-0.43926100	-0.89978700
C	-1.96212300	-1.08445700	-0.05920600	O	0.36733200	0.04526200	1.37412500
C	-2.59921100	0.08079300	-0.51344300	O	-0.36733000	0.04529100	-1.37412600
C	-3.93254500	0.31749700	-0.16617400	H	-0.34566000	-2.00525500	-1.18799000
C	-4.61035300	-0.61135100	0.62490700	H	-2.13654900	-2.92524100	1.07820100
H	-4.50207700	-2.48809200	1.68142700	H	2.13655700	-2.92521900	-1.07826100
H	-4.43947700	1.21549700	-0.51081200	B	1.51840800	0.81592900	1.35681000
H	-5.64781500	-0.43928800	0.89977200	B	-1.51840800	0.81595500	-1.35680100
C	-0.52993200	-1.12239000	-0.55955800	O	-1.62487000	2.00285600	-1.99723700
C	0.52993600	-1.12240100	0.55952900	O	1.62485600	2.00282500	1.99726000
H	0.34566600	-2.00527900	1.18794300	C	-0.53654800	2.55355800	-2.73670300
C	1.96212700	-1.08445500	0.05917700	H	-0.48922400	3.62565200	-2.52291100
C	2.62895100	-2.01989900	-0.72961000	H	0.41401000	2.08328800	-2.46926700
C	2.59921200	0.08078900	0.51343500	H	-0.71744900	2.41592200	-3.80872200
C	3.96160300	-1.77149800	-1.06811100	C	0.53654200	2.55343900	2.73680200
C	3.93254500	0.31750200	0.16617100	H	0.48990300	3.62574600	2.52394200
C	4.61035500	-0.61133100	-0.62492600	H	-0.41416200	2.08392300	2.46855400
H	4.50208500	-2.48805300	-1.68147800	H	0.71689800	2.41474700	3.80877800

Bisbenzoxaborol coordinated to methylpyruvate orientation 1

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.347332 (Hartree/Particle)
Thermal correction to Energy= 0.372165
Thermal correction to Enthalpy= 0.373109
Thermal correction to Gibbs Free Energy= 0.290949
Sum of electronic and zero-point Energies= -1272.909731
Sum of electronic and thermal Energies= -1272.884897
Sum of electronic and thermal Enthalpies= -1272.883953
Sum of electronic and thermal Free Energies= -1272.966114

C	5.42102100	0.40583200	0.13440100	H	1.76320500	1.72819700	-1.61916900
C	4.26666000	1.15497700	-0.10685000	H	4.29377500	2.23996500	-0.03111500
C	3.09680200	0.47620900	-0.44167900	H	-0.03344400	3.73089100	-1.49166500
C	3.06165900	-0.92336700	-0.54212100	B	-0.35340900	0.73499900	1.86305300
C	4.22420500	-1.66017900	-0.29769300	B	1.59509300	-1.25608800	-0.93879800
C	5.40202500	-0.99191000	0.04007500	O	1.01428700	-2.46814100	-1.12401900
H	6.34536300	0.91390100	0.39766100	O	-0.65280600	-0.15787700	2.84320900
H	4.21319700	-2.74488300	-0.37094900	C	-1.45969500	-3.17118100	1.29335200
H	6.31222200	-1.55440200	0.23154000	H	-1.37431200	-3.25487800	2.37730600
C	1.72903100	1.05340400	-0.75185600	H	-1.80271300	-4.12137600	0.86459700
C	1.08082600	1.82927400	0.41609600	H	-0.47723700	-2.96812500	0.85258800
H	1.74205500	2.66765300	0.67522800	C	-2.42672500	-2.07654600	0.94579700
C	-0.32948400	2.28980000	0.10279900	C	-2.61535000	-1.80373000	-0.56685900
C	-0.74661200	3.21114800	-0.85534300	O	-3.02017100	-1.39016600	1.75447400
C	-1.24559700	1.61976800	0.92914700	O	-1.83858700	-2.20489700	-1.41538800
C	-2.11550100	3.46116400	-0.98404300	O	-3.69777000	-1.07868000	-0.81102900
C	-2.61437800	1.87124800	0.78186300	C	-3.89649600	-0.68978400	-2.18718800
C	-3.04413300	2.79435800	-0.17427800	H	-4.84462600	-0.15408200	-2.19929500
H	-2.46316700	4.18249400	-1.71951500	H	-3.07903000	-0.03992200	-2.50704500
H	-3.34360000	1.34775600	1.39480400	H	-3.93773000	-1.57329600	-2.82836200
H	-4.10472000	3.00356200	-0.28951600	H	-1.60530100	-0.32940200	2.90579600
O	0.97122200	0.96827900	1.55061000	H	0.06931800	-2.39784300	-1.36248100
O	0.89742200	-0.06522700	-1.08728400				

Bisbenzoxaborol coordinated to methylpyruvate orientation 2

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opt=calcfc freq=noraman b3lyp/6-31g(d,p)

Zero-point correction= 0.347075 (Hartree/Particle)
Thermal correction to Energy= 0.371804
Thermal correction to Enthalpy= 0.372748
Thermal correction to Gibbs Free Energy= 0.290791
Sum of electronic and zero-point Energies= -1272.945969
Sum of electronic and thermal Energies= -1272.921240
Sum of electronic and thermal Enthalpies= -1272.920296
Sum of electronic and thermal Free Energies= -1273.002253

C	5.53816300	-0.02568600	0.55068500	C	5.43265200	-1.40528000	0.33191300
C	4.47390900	0.82898900	0.25363300	H	6.45933200	0.38461900	0.95519300
C	3.30534500	0.27367500	-0.26368900	H	4.17946400	-3.01987900	-0.35718600
C	3.18445800	-1.10594900	-0.49049100	H	6.27357300	-2.05083500	0.56925800
C	4.25736100	-1.94929100	-0.18784000	C	2.02849400	0.98090700	-0.67664900

C	1.31344300	1.74156700	0.46166000
H	2.02543900	2.46482100	0.88251400
C	0.02895900	2.41425400	0.01669200
C	-0.13428800	3.45645200	-0.89342400
C	-1.06783000	1.82744200	0.66603800
C	-1.42798600	3.91596800	-1.15148600
C	-2.35772200	2.29693200	0.39710900
C	-2.53349700	3.34186300	-0.51137600
H	-1.57833900	4.73052500	-1.85448900
H	-3.21957000	1.85622700	0.89258000
H	-3.53011800	3.71882200	-0.72367400
O	0.93918900	0.81685800	1.48608200
O	1.15875900	-0.03931900	-1.18032200
H	2.21985300	1.70296100	-1.48344900
H	4.56810900	1.89852000	0.42565300
H	0.71667400	3.91151100	-1.39428600
B	-0.43458400	0.74558200	1.59929600
B	1.74860500	-1.29068000	-1.06272600
O	1.11249300	-2.43644300	-1.40567600
O	-0.99034600	-0.18337500	2.42265500
C	-1.38612500	-3.03356300	0.80202300
H	-0.52079900	-3.52881800	0.36197100
H	-1.05753600	-2.35366400	1.59651700
H	-2.06338000	-3.76495300	1.25791700
C	-2.11049900	-2.24636400	-0.24865400
C	-3.40348900	-1.52947400	0.19877200
O	-1.73451700	-2.08423300	-1.39461700
O	-3.51115500	-0.95041600	1.26628100
O	-4.35119600	-1.59749900	-0.72780900
C	-5.57928100	-0.89648200	-0.43254900
H	-6.25332800	-1.13836300	-1.25216800
H	-5.98832700	-1.23123400	0.52276800
H	-5.39240300	0.17856600	-0.39136500
H	-1.95088200	-0.25652700	2.30843200
H	0.18393400	-2.29715200	-1.66598700

Bisbenzoxaborol coordinated to ethylacetoacetate orientation 1

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.405070 (Hartree/Particle)
Thermal correction to Energy= 0.432146
Thermal correction to Enthalpy= 0.433091
Thermal correction to Gibbs Free Energy= 0.345490
Sum of electronic and zero-point Energies= -1351.500457
Sum of electronic and thermal Energies= -1351.473381
Sum of electronic and thermal Enthalpies= -1351.472437
Sum of electronic and thermal Free Energies= -1351.560037

C	-0.59189200	-3.34995200	0.87740300
H	-1.02298100	-4.25254800	1.32558600
H	-0.13211100	-2.76519900	1.68514300
H	0.17385700	-3.60409100	0.14381700
C	-1.65960600	-2.48765300	0.25590800
C	-3.70420200	-1.07844900	0.72787700
O	-1.54194800	-1.92624600	-0.82027200
O	-4.59798000	-1.26330600	-0.24062800
C	-5.29602200	-0.08005700	-0.71731300
H	-5.85673300	0.34945700	0.11852700
H	-4.54803300	0.65114100	-1.03634400
C	-6.19841500	-0.51592200	-1.85447200
H	-6.92829200	-1.25795400	-1.51551500
H	-6.74352000	0.35074900	-2.24342400
H	-5.61363600	-0.95061700	-2.67081900
O	-3.50038600	-0.00205000	1.26969700
C	-0.37768200	4.48086300	-0.77052200
C	0.80648100	3.77725600	-0.53646400
C	0.73958900	2.59566800	0.19925500
C	-0.47644200	2.10922800	0.70056100
C	-1.65629400	2.81908600	0.45261000
C	-1.60130500	4.00535600	-0.28159300
H	-0.34885100	5.40785500	-1.33786300
H	-2.60956600	2.45035900	0.82328500
H	-2.51087800	4.56825900	-0.47612900
C	1.86765900	1.65374500	0.57339400
C	2.50860100	0.96617700	-0.65607000
H	2.77328100	1.75426300	-1.37526900
C	3.70436200	0.08553000	-0.34786100
C	4.92991100	0.45215600	0.20520600
C	3.43375700	-1.23955800	-0.72215000
C	5.89902100	-0.53820800	0.38473400
C	4.41102500	-2.22108400	-0.53287700
C	5.64344800	-1.86618600	0.01819300
H	6.86308600	-0.27508100	0.81292800
H	4.21603100	-3.25311400	-0.81468900
H	6.41233300	-2.62035000	0.16589600
O	1.53499400	0.11012200	-1.26172100
O	1.28773800	0.65989300	1.42245100
H	2.66327800	2.16860400	1.12937700
H	1.75170400	4.15430600	-0.92166500
H	5.13991400	1.48048300	0.49224600
B	1.97089100	-1.20628700	-1.25593000
B	-0.08669300	0.80779900	1.47296300
O	-0.84178600	-0.11021900	2.13506900
O	1.18358900	-2.24398700	-1.63320800
H	-1.79614300	0.08178400	2.03497300
H	0.23730100	-1.99830500	-1.67780400

C	-2.95553000	-2.34652700	1.07185700
H	-3.57609700	-3.22477300	0.85659400
H	-2.71749700	-2.34526900	2.13880900

ss

Bisbenzoxaborol coordinated to ethylacetoacetate orientation 2

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.404385 (Hartree/Particle)
Thermal correction to Energy= 0.431870
Thermal correction to Enthalpy= 0.432814
Thermal correction to Gibbs Free Energy= 0.343372
Sum of electronic and zero-point Energies= -1351.498268
Sum of electronic and thermal Energies= -1351.470783
Sum of electronic and thermal Enthalpies= -1351.469839
Sum of electronic and thermal Free Energies= -1351.559281

C	-5.82057500	0.34193300	-0.37966200	C	2.38493300	1.13053700	-0.57623300
H	-6.59527400	-0.41268800	-0.55599100	H	2.69577700	1.95741600	-1.23011000
H	-5.72829400	0.93078200	-1.30175600	C	3.55034100	0.21880500	-0.24263200
H	-6.11645600	1.00313000	0.43686400	C	4.75160200	0.54358500	0.38467400
C	-4.48651700	-0.29968900	-0.06658500	C	3.27325800	-1.08895200	-0.66903200
C	-2.63699300	-1.89508800	-0.83104900	C	5.69072100	-0.47156000	0.58472600
O	-3.78767900	0.10399400	0.84621100	C	4.21987400	-2.09557000	-0.45827900
O	-2.47347100	-2.70564100	0.20960600	C	5.42854800	-1.78271700	0.16632000
C	-1.11677800	-3.17103600	0.49572000	H	6.63611700	-0.24109200	1.06969200
H	-0.74677500	-3.70576900	-0.38297000	H	4.01956900	-3.11482700	-0.78002800
H	-0.49246900	-2.29475700	0.66756900	H	6.17362300	-2.55700200	0.33128000
C	-1.20195800	-4.05147300	1.72480300	O	1.44127400	0.32047700	-1.28268100
H	-1.87010300	-4.90366400	1.56145400	O	1.05396500	0.69117500	1.39898000
H	-0.20466200	-4.43488500	1.96487600	H	2.43799900	2.21864900	1.29088500
H	-1.56306000	-3.47714700	2.58322800	H	1.63456000	4.35621000	-0.63028200
O	-1.76624600	-1.53163400	-1.60052900	H	4.96585800	1.55867400	0.71300600
C	-0.50204900	4.66732000	-0.58262000	B	1.84336700	-1.00870300	-1.28337800
C	0.66966100	3.94629600	-0.33883500	B	-0.32418900	0.80691800	1.34060000
C	0.56583200	2.70594200	0.28746700	O	-1.09571000	-0.19957100	1.82650100
C	-0.67596200	2.17405100	0.66617200	O	1.05725300	-2.01713900	-1.72789100
C	-1.84107600	2.90641800	0.41578500	H	-2.04087100	-0.07579800	1.62707900
C	-1.74943200	4.15275700	-0.20699900	H	0.13054300	-1.74024900	-1.87014800
H	-0.44434200	5.64029000	-1.06432100	C	-4.08662000	-1.46525800	-0.97201800
H	-2.81204800	2.51335700	0.70756200	H	-4.75075000	-2.30574700	-0.73230900
H	-2.64836400	4.73303300	-0.40033400	H	-4.26944100	-1.18562600	-2.01460900
C	1.67617000	1.74258900	0.65855300				

Conia-ene pro-S TS coordination mode 1

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.494799 (Hartree/Particle)
Thermal correction to Energy= 0.526588
Thermal correction to Enthalpy= 0.527533
Thermal correction to Gibbs Free Energy= 0.429742
Sum of electronic and zero-point Energies= -1545.430387

Sum of electronic and thermal Energies= -1545.398597
Sum of electronic and thermal Enthalpies= -1545.397653
Sum of electronic and thermal Free Energies= -1545.495444

C	1.64232300	-3.48591500	0.33381000	C	-2.09528200	3.50562000	1.30584700
H	0.61979600	-3.70969400	0.01624100	C	-1.98515200	2.54793900	0.30004200
H	1.69374800	-3.68186800	1.41328500	C	-0.74911100	2.22559400	-0.27999400
H	2.33158000	-4.16431400	-0.17326500	C	0.40514800	2.88179700	0.15916900
C	1.92386200	-2.03021800	0.04936300	C	0.30781500	3.84789800	1.16460700
C	3.19428200	-1.52326300	-0.25493300	H	-0.99785300	4.91635500	2.50888700
C	3.31699300	-0.21034400	-0.93542400	H	1.37080100	2.64333300	-0.27975400
O	0.92947000	-1.21575100	0.24936400	H	1.19820200	4.37082800	1.50629800
O	4.61452600	0.17152800	-1.06946000	C	-3.07324500	1.68367200	-0.30831400
C	4.44567700	-2.34967400	-0.03556200	C	-3.57828300	0.61064600	0.69456600
H	4.29476700	-3.39176000	-0.33590500	H	-3.92684800	1.12542400	1.60063400
H	5.26043400	-1.95840400	-0.64606800	C	-4.63093600	-0.32760900	0.13692600
C	4.85190600	-2.30697900	1.45913800	C	-5.93251000	-0.02838300	-0.26001100
H	4.21563200	-2.98587000	2.03933300	C	-4.11658200	-1.63174000	0.05054700
H	5.88824400	-2.63718000	1.59626200	C	-6.73137600	-1.06454200	-0.75070000
C	4.68601000	-0.87781100	2.01465200	C	-4.92490800	-2.65658000	-0.44879300
H	5.36081600	-0.19338800	1.48686100	C	-6.23283200	-2.37030600	-0.84441100
H	4.95784800	-0.85491800	3.07977300	H	-7.75150000	-0.85497200	-1.06314800
C	3.30597800	-0.38756300	1.90796500	H	-4.54055100	-3.67058600	-0.52925000
C	2.16181300	0.10391600	2.04284000	H	-6.87112900	-3.16134300	-1.23010600
H	1.60758100	0.73691600	2.72051500	O	-2.46265400	-0.21679800	1.03635400
C	4.84337600	1.40110200	-1.79656400	O	-2.47209900	1.01328100	-1.41303600
H	4.36691200	1.32361300	-2.77825500	H	-3.93278400	2.26851900	-0.66255000
H	4.36086000	2.22361200	-1.25896200	H	-3.05653000	3.75251900	1.75251400
C	6.34440500	1.59408400	-1.90339600	H	-6.32850800	0.98293200	-0.19307100
H	6.81018800	0.76063900	-2.43907700	B	-2.64948400	-1.50870500	0.56037900
H	6.55989100	2.51776900	-2.45119300	B	-1.08938600	1.14862400	-1.37101200
H	6.80486500	1.66901900	-0.91261900	O	-0.31651700	0.40869000	-2.19258400
O	2.41547700	0.48599100	-1.38190100	O	-1.64473800	-2.41759700	0.55973000
H	1.37629300	-0.39090800	1.04242100	H	0.62623100	0.44460800	-1.94245400
C	-0.93454100	4.15769300	1.73239900	H	-0.78134700	-1.96944200	0.67546600

Conia-ene pro-S precomplex coordination mode 1

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.500282 (Hartree/Particle)
Thermal correction to Energy= 0.533323
Thermal correction to Enthalpy= 0.534267
Thermal correction to Gibbs Free Energy= 0.432226
Sum of electronic and zero-point Energies= -1545.472808
Sum of electronic and thermal Energies= -1545.439767
Sum of electronic and thermal Enthalpies= -1545.438823
Sum of electronic and thermal Free Energies= -1545.540864

C	-1.96654300	-3.42053600	-1.37564300	O	-0.83474800	-1.72905800	-0.21731100
H	-1.23388300	-4.13577800	-0.98436700	O	-4.25104500	-0.13770000	1.47578900
H	-1.60079000	-3.08796300	-2.35462700	C	-4.57840000	-2.29896400	-0.22164900
H	-2.92074600	-3.92732900	-1.51444000	H	-4.52777500	-3.39368900	-0.24200600
C	-2.05207100	-2.24307300	-0.45170500	H	-5.25445000	-2.05097400	0.60146600
C	-3.20451200	-1.73013400	0.09037500	C	-5.21875200	-1.83106000	-1.54726500
C	-3.08840100	-0.56769900	0.96309000	H	-4.57582300	-2.10665800	-2.39210800

H	-6.16099200	-2.37995000	-1.67539600
C	-5.54551900	-0.32191300	-1.64200000
H	-6.10955100	-0.01715000	-0.75014300
H	-6.21749500	-0.16634700	-2.49707800
C	-4.37774500	0.54782300	-1.80508900
C	-3.41728000	1.26288500	-1.96948800
H	-2.54384000	1.86443500	-2.09166100
C	-4.20326500	1.03081500	2.32858000
H	-3.52685700	0.82975800	3.16493800
H	-3.79291100	1.86534600	1.75186900
C	-5.61912800	1.30707200	2.79699700
H	-6.01919400	0.45708200	3.35879300
H	-5.62588800	2.18580700	3.45069500
H	-6.28098800	1.50580700	1.94803400
O	-2.01717300	0.00209500	1.24427300
H	-0.94379600	-0.94527600	0.38976000
C	0.77047400	3.95075700	-1.92002400
C	1.95936400	3.32322400	-1.53978700
C	1.93466800	2.46618700	-0.44108700
C	0.75364000	2.21835300	0.27412100
C	-0.43113800	2.84723600	-0.12178500
C	-0.41797400	3.71691800	-1.21530700
H	0.76821700	4.63196300	-2.76723500
H	-1.35927300	2.66245200	0.41374900
H	-1.33018700	4.22570100	-1.51875800
C	3.07500100	1.66581500	0.15791000
C	3.55016800	0.52328000	-0.77490200
H	3.79763700	0.96602700	-1.75010900
C	4.70218300	-0.29814800	-0.22920800
C	6.00059800	0.11762200	0.05908100
C	4.29541600	-1.62728700	-0.03600700
C	6.90436000	-0.82621600	0.55368300
C	5.20868400	-2.55972800	0.46397000
C	6.51284600	-2.15618000	0.75550100
H	7.92318000	-0.52489200	0.78452800
H	4.90746400	-3.59200100	0.62475400
H	7.23194100	-2.87370400	1.14254800
O	2.46467100	-0.39234400	-0.95393300
O	2.56254400	1.08929500	1.35923700
H	3.94038600	2.29540300	0.40480100
H	2.87774100	3.51183600	-2.09191000
H	6.31555900	1.14795700	-0.09362500
B	2.79771000	-1.64918500	-0.46163000
B	1.19024400	1.25041200	1.42586200
O	0.48602400	0.60081800	2.38566100
O	1.90511500	-2.66390500	-0.38700500
H	-0.47293000	0.67229900	2.25005600
H	0.99234000	-2.36217800	-0.55155000

Conia-ene pro-S product coordination mode 1

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.502848 (Hartree/Particle)
Thermal correction to Energy= 0.534423
Thermal correction to Enthalpy= 0.535367
Thermal correction to Gibbs Free Energy= 0.438372
Sum of electronic and zero-point Energies= -1545.524785
Sum of electronic and thermal Energies= -1545.493210
Sum of electronic and thermal Enthalpies= -1545.492266
Sum of electronic and thermal Free Energies= -1545.589260

C	1.05425700	-2.73711800	-0.26476400
H	0.38399300	-3.12476600	0.50361600
H	1.75673600	-3.50726100	-0.59215900
H	0.44423200	-2.43673900	-1.12597100
C	1.75797300	-1.50630900	0.25046300
C	3.09043200	-1.07260300	-0.41647800
C	3.17569000	0.45018800	-0.23154900
O	1.32647900	-0.85336600	1.19066500
O	3.82262900	0.83555800	0.86010100
C	3.20992600	-1.42910300	-1.93720600
H	2.23680700	-1.59761200	-2.40244300
H	3.65419700	-0.57449600	-2.45613500
C	4.15570700	-2.64251700	-2.02375000
H	3.60130400	-3.58068700	-1.90223000
H	4.67030400	-2.69334700	-2.98857400
C	5.11345700	-2.44443800	-0.83791800
H	5.88288300	-1.70415400	-1.10630900
H	5.63400700	-3.35561600	-0.52710400
C	4.22559800	-1.88154100	0.25185900
C	4.33913300	-2.11136900	1.55996900
H	5.14779300	-2.72298100	1.95214200
C	3.81323100	2.25924200	1.15378000
H	4.29759300	2.78596700	0.32582000
H	2.77186200	2.58937500	1.20496600
C	4.54570200	2.45196600	2.46677200
H	5.57844900	2.09611600	2.39656300
H	4.56372400	3.51636800	2.72460600
H	4.04539100	1.90979100	3.27490800
O	2.66738600	1.23423500	-1.02242400
H	3.64792900	-1.68781400	2.28152200
C	-1.75174400	4.77098800	0.17058800
C	-2.65272300	3.71438600	0.01608500
C	-2.18703600	2.52295800	-0.53676900
C	-0.85067800	2.36814600	-0.93247300

C	0.04311500	3.43192100	-0.76691000	H	-7.07515200	-2.18745900	-0.82619600
C	-0.41270800	4.63163300	-0.21669600	H	-3.72100300	-3.93439800	1.22887800
H	-2.09416500	5.71196300	0.59410800	H	-5.94642800	-4.16496100	0.14258900
H	1.08449000	3.32583700	-1.06007400	O	-2.26562400	0.13692100	1.24890100
H	0.27130200	5.46711600	-0.08914400	O	-2.05242800	0.37151000	-1.48241800
C	-2.95396700	1.23996800	-0.79155400	H	-3.83607800	1.40692400	-1.42481500
C	-3.42103300	0.55336500	0.51504300	H	-3.69073800	3.83209700	0.32056700
H	-3.95933300	1.30454100	1.11023100	H	-6.01324500	0.05209000	-0.72550200
C	-4.26127800	-0.69380500	0.31711000	B	-2.26163700	-1.24039400	1.41432300
C	-5.50670500	-0.81057400	-0.29746000	B	-0.78189300	0.91843100	-1.51417200
C	-3.60860400	-1.80501100	0.87242400	O	0.25480200	0.19128100	-2.01048600
C	-6.10310300	-2.07290500	-0.35286900	O	-1.20946800	-1.91495600	1.93844200
C	-4.21511600	-3.06269400	0.80637900	H	1.10596200	0.65806000	-1.89092900
C	-5.46369900	-3.19237100	0.19581000	H	-0.39033000	-1.37803100	1.95475000

Conia-ene pro-S TS coordination mode 2

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.494810 (Hartree/Particle)
Thermal correction to Energy= 0.526619
Thermal correction to Enthalpy= 0.527563
Thermal correction to Gibbs Free Energy= 0.429199
Sum of electronic and zero-point Energies= -1545.428031
Sum of electronic and thermal Energies= -1545.396223
Sum of electronic and thermal Enthalpies= -1545.395278
Sum of electronic and thermal Free Energies= -1545.493642

C	3.79661600	2.82344900	-1.39539500	O	1.76904200	0.06691800	1.34196100
H	3.16210400	3.71449900	-1.39810400	H	1.58343700	0.52351100	-1.28360000
H	3.97071200	2.54830000	-2.44404100	C	-3.13536800	4.01121400	1.91882200
H	4.75771800	3.07318200	-0.94009000	C	-3.73512100	2.84445700	1.43723900
C	3.06006800	1.71720500	-0.67435800	C	-3.12234100	2.17326200	0.38177400
C	3.70015400	0.68156800	0.01964700	C	-1.93254600	2.64087200	-0.19648200
C	2.92591100	-0.12493700	0.99517900	C	-1.33894900	3.80403000	0.30158500
O	1.77731000	1.68374200	-0.86311300	C	-1.94352500	4.48756800	1.35809900
O	3.66798300	-1.13556300	1.52317600	H	-3.59872700	4.55515100	2.73825400
C	5.18544300	0.42538100	-0.13053400	H	-0.40932100	4.17685900	-0.12336100
H	5.75443900	1.36110100	-0.15370900	H	-1.49083900	5.39463800	1.75057800
H	5.55031800	-0.14636400	0.72396300	C	-3.54646100	0.88207700	-0.29116400
C	5.45934800	-0.36408900	-1.43661000	C	-3.40356000	-0.34101300	0.64708300
H	5.42198500	0.31363400	-2.29809800	H	-4.03313400	-0.15879700	1.52973500
H	6.45912300	-0.81418900	-1.42255200	C	-3.72373600	-1.67535900	0.00049000
C	4.39904700	-1.46746600	-1.63050200	C	-4.93796800	-2.11490300	-0.52303500
H	4.46230600	-2.19253200	-0.81044700	C	-2.58000800	-2.48949400	-0.00990700
H	4.59256700	-2.01108100	-2.56662100	C	-4.99891400	-3.39946900	-1.06940400
C	3.03350100	-0.93656900	-1.71097800	C	-2.65527300	-3.77108900	-0.56251200
C	1.84341900	-0.62357200	-1.93915700	C	-3.86625700	-4.22362600	-1.08960100
H	0.98803400	-0.93379800	-2.52131700	H	-5.93633900	-3.76389900	-1.48239000
C	3.00741100	-1.95916400	2.51444800	H	-1.77841800	-4.41418300	-0.58033600
H	2.63449400	-1.31319100	3.31520300	H	-3.93602300	-5.22018500	-1.51855200
H	2.14632500	-2.44896100	2.04985500	O	-2.04119800	-0.42970100	1.07304300
C	4.02653500	-2.96221300	3.02163800	O	-2.66845400	0.71287500	-1.40632100
H	4.88456800	-2.45627000	3.47634500	H	-4.58132800	0.91814100	-0.65785600
H	3.56550800	-3.60592600	3.77849700	H	-4.65828400	2.47988300	1.88320900
H	4.39111500	-3.59883600	2.20857500	H	-5.82384000	-1.48320100	-0.51215700

B	-1.46815600	-1.62214300	0.65610300
B	-1.63687900	1.63205000	-1.35236900
O	-0.62027200	1.54246200	-2.25175600
O	-0.15557100	-1.90446300	0.82638600
H	0.14513900	2.07560000	-1.97819800
H	0.36623800	-1.14150800	1.15334600

Conia-ene pro-S precomplex coordination mode 2

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.500589 (Hartree/Particle)
Thermal correction to Energy= 0.533376
Thermal correction to Enthalpy= 0.534320
Thermal correction to Gibbs Free Energy= 0.433772
Sum of electronic and zero-point Energies= -1545.475177
Sum of electronic and thermal Energies= -1545.442390
Sum of electronic and thermal Enthalpies= -1545.441446
Sum of electronic and thermal Free Energies= -1545.541994

C	3.84535500	2.89673400	-1.15772700
H	3.59309000	3.90532200	-0.81305500
H	3.47881600	2.80350800	-2.18793300
H	4.92905600	2.78126800	-1.16796200
C	3.16114000	1.88832100	-0.28549300
C	3.74101500	0.76548100	0.24266900
C	2.89841300	-0.13342000	1.03010600
O	1.86382100	2.20643100	-0.09894800
O	3.52055600	-1.23680700	1.45797100
C	5.18211400	0.37873900	-0.04412800
H	5.82887300	1.26013200	0.04452000
H	5.51643000	-0.31313200	0.73325300
C	5.44158500	-0.26361000	-1.42618600
H	5.23113700	0.46181800	-2.22156900
H	6.51252500	-0.49748900	-1.48953400
C	4.65376800	-1.56140400	-1.72427300
H	4.78031900	-2.26404500	-0.88967700
H	5.10416300	-2.04485100	-2.60201300
C	3.22666900	-1.34922800	-1.98164000
C	2.05540000	-1.15566600	-2.21010700
H	1.02720600	-0.91474100	-2.37681500
C	2.75018400	-2.18961600	2.23898900
H	2.29512800	-1.65982300	3.08133600
H	1.94966500	-2.58785700	1.61129700
C	3.70930400	-3.27042700	2.69862100
H	4.51152800	-2.85091100	3.31432200
H	3.16630900	-4.01032200	3.29623100
H	4.15957700	-3.78548600	1.84397900
O	1.70333300	0.09022600	1.31112900
H	1.47692000	1.50008200	0.49699600
C	-3.25180500	4.21211500	1.48161000
C	-3.81935300	3.02944700	0.99921300
C	-3.07240600	2.24778500	0.12137800
C	-1.77919200	2.61910500	-0.27823100
C	-1.21990300	3.80028900	0.21979900
C	-1.96045100	4.59455500	1.09790600
H	-3.81927500	4.84227500	2.16188100
H	-0.21368900	4.09952200	-0.06422600
H	-1.53624700	5.51665100	1.48704700
C	-3.44160100	0.91841900	-0.50695900
C	-3.47464400	-0.22745500	0.53664000
H	-4.17305600	0.06204100	1.33407000
C	-3.80967400	-1.59170200	-0.03418900
C	-4.99388500	-2.00965900	-0.63795000
C	-2.71754600	-2.45955400	0.12269200
C	-5.07657900	-3.32835600	-1.09243200
C	-2.81259300	-3.77448500	-0.34135100
C	-3.99458800	-4.20617100	-0.94569700
H	-5.99126300	-3.67725500	-1.56531200
H	-1.97366200	-4.45768400	-0.23317700
H	-4.08038200	-5.22767900	-1.30744000
O	-2.16467600	-0.34979700	1.10144400
O	-2.41114400	0.63238200	-1.45542300
H	-4.40769200	0.94823400	-1.02760800
H	-4.82193000	2.73862200	1.30609900
H	-5.83993700	-1.33600000	-0.75769200
B	-1.62189100	-1.59424600	0.81237600
B	-1.34763000	1.49629900	-1.27747900
O	-0.18027700	1.26111200	-1.93540400
O	-0.33714000	-1.91270600	1.09838300
H	0.53633900	1.83123700	-1.60815400
H	0.20751700	-1.14186400	1.35387200

Conia-ene pro-S product coordination mode 2

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opt=(calcfc,ts,noeigen) freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.502177 (Hartree/Particle)
Thermal correction to Energy= 0.534101
Thermal correction to Enthalpy= 0.535045
Thermal correction to Gibbs Free Energy= 0.436634
Sum of electronic and zero-point Energies= -1545.525293
Sum of electronic and thermal Energies= -1545.493369
Sum of electronic and thermal Enthalpies= -1545.492425
Sum of electronic and thermal Free Energies= -1545.590836

C	-5.13957200	0.30474100	1.55112300	C	1.76028100	2.65062200	0.28828500
H	-5.18143200	0.91458800	2.45536600	C	0.52770900	2.30700300	0.86283400
H	-5.51266000	-0.70205600	1.76875500	C	-0.55351200	3.18701800	0.74517600
H	-5.79884600	0.71800700	0.78029900	C	-0.39044300	4.38940000	0.05369100
C	-3.70741800	0.22568200	1.07519300	H	0.96019900	5.65363300	-1.05480600
C	-3.39719500	-0.33224600	-0.33421900	H	-1.51221700	2.94561300	1.19856300
C	-2.11580300	-1.18354400	-0.30391100	H	-1.22221400	5.08374700	-0.03654800
O	-2.80559300	0.65979800	1.77581600	C	2.77841800	1.55927800	0.55712500
O	-2.07801600	-1.97605400	0.76629600	C	3.23645800	0.81990200	-0.72509600
C	-3.24052000	0.88024100	-1.31126600	H	3.56455600	1.57621200	-1.45192600
H	-2.89638900	1.78397400	-0.80140000	C	4.30757300	-0.22809000	-0.49067600
H	-2.46973100	0.60556600	-2.03725900	C	5.61234700	-0.04590500	-0.03633600
C	-4.60415300	1.02562700	-2.00396800	C	3.80961700	-1.50114500	-0.80674700
H	-5.31036300	1.57760400	-1.37063600	C	6.42945700	-1.17101800	0.10101500
H	-4.52884300	1.57025100	-2.95025300	C	4.63655100	-2.61846600	-0.66020600
C	-5.06833300	-0.42917600	-2.18748700	C	5.94668100	-2.44923400	-0.20879000
H	-4.61099900	-0.84836000	-3.09497000	H	7.45196600	-1.05308400	0.45124200
H	-6.15255000	-0.53920100	-2.29623800	H	4.26502600	-3.61248500	-0.89757300
C	-4.53036000	-1.16682200	-0.97162900	H	6.59984200	-3.31079100	-0.09496000
C	-4.94497700	-2.35616800	-0.53153000	O	2.11340700	0.12062000	-1.26936300
H	-5.75319800	-2.88869000	-1.02684900	O	2.13309100	0.62222100	1.42090900
C	-0.92597900	-2.86419500	0.90815100	H	3.67093600	1.95142500	1.06390100
H	-1.01129100	-3.64403800	0.14483600	H	2.89192900	4.10968400	-0.85150000
H	-0.02199100	-2.28657000	0.72032400	H	5.99776900	0.94233600	0.20647000
C	-0.95832800	-3.41646600	2.31766700	B	2.33598900	-1.25011900	-1.24616800
H	-1.89280600	-3.95145100	2.51833000	B	0.78768800	0.92280000	1.54531800
H	-0.12564900	-4.11527800	2.45145500	O	-0.04098900	0.04931900	2.17088700
H	-0.84492200	-2.60491200	3.04173300	O	1.37639800	-2.15967000	-1.53713300
O	-1.28391600	-1.17015100	-1.19203400	H	-0.97511200	0.32426900	2.11624600
H	-4.48810800	-2.84576900	0.32349700	H	0.48714900	-1.76089100	-1.61013000
C	0.84516900	4.71346000	-0.52111900				
C	1.93408500	3.84526500	-0.40806800				

Conia-ene uncatalyzed TS

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.247671 (Hartree/Particle)
Thermal correction to Energy= 0.262433
Thermal correction to Enthalpy= 0.263378
Thermal correction to Gibbs Free Energy= 0.206006
Sum of electronic and zero-point Energies= -654.118726
Sum of electronic and thermal Energies= -654.103964
Sum of electronic and thermal Enthalpies= -654.103020
Sum of electronic and thermal Free Energies= -654.160391

C	3.02793400	-0.38830100	-1.34038100	C	0.32344300	2.00741500	1.09693200
H	3.72542700	-1.22918400	-1.36007300	H	-0.77342200	2.00912300	1.08150900
H	3.53902300	0.45347300	-0.85419900	H	0.64539800	2.76470100	1.82559800
H	2.78999700	-0.09164100	-2.36592600	C	0.80434100	0.69668600	1.56612700
C	1.80540600	-0.80430900	-0.55225800	C	1.24249800	-0.26424400	2.24331400
C	0.57587900	-0.12560500	-0.61568800	H	1.50264700	-0.48572000	3.26766900
C	-0.66327500	-0.85393200	-0.22257500	C	-3.02762100	-0.69870800	-0.05357100
O	1.99181100	-1.74300400	0.31641200	H	-3.15663600	-1.57080200	-0.70292600
O	-1.77296300	-0.06171300	-0.36719100	H	-2.99461900	-1.06321900	0.97830500
C	0.45745900	1.22383900	-1.29637200	C	-4.12610400	0.32849900	-0.25994400
H	1.09346600	1.28129400	-2.18656700	H	-4.14168200	0.68399800	-1.29555400
H	-0.56982200	1.38216100	-1.62717800	H	-5.10109800	-0.11781000	-0.03511300
C	0.86104900	2.34570000	-0.30554300	H	-3.98539100	1.19260000	0.39819100
H	1.95395300	2.42486300	-0.25358300	O	-0.74979200	-2.00288500	0.16026100
H	0.48061600	3.32109000	-0.63116700	H	1.55363300	-1.29635600	1.32490800

Conia-ene uncatalyzed precomplex

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.253074 (Hartree/Particle)
Thermal correction to Energy= 0.268969
Thermal correction to Enthalpy= 0.269913
Thermal correction to Gibbs Free Energy= 0.208964
Sum of electronic and zero-point Energies= -654.167899
Sum of electronic and thermal Energies= -654.152005
Sum of electronic and thermal Enthalpies= -654.151060
Sum of electronic and thermal Free Energies= -654.212010

C	3.45777400	-0.24858100	-0.44416400	C	-0.42987800	2.55541000	0.13467800
H	4.09748100	-1.03652600	-0.85801400	H	-1.35135800	2.33150900	-0.41897900
H	3.94187700	0.10536800	0.47372500	H	-0.44355100	3.63688500	0.32883900
H	3.40449300	0.57804600	-1.15193400	C	-0.45775200	1.85937700	1.42359900
C	2.11531400	-0.82789300	-0.10335700	C	-0.47939300	1.31337400	2.50133700
C	0.90449900	-0.35236600	-0.54905300	H	-0.48544000	0.82711700	3.45017600
C	-0.29420300	-1.04564900	-0.08818800	C	-2.66386200	-1.15617800	-0.08965100
O	2.24083700	-1.88250600	0.70776500	H	-2.63785900	-2.22292800	-0.33226500
O	-1.44852500	-0.53720600	-0.56670400	H	-2.69773300	-1.06162600	1.00000700
C	0.77676900	0.85767600	-1.45656100	C	-3.82711300	-0.44821700	-0.75860400
H	1.58740800	0.85098900	-2.19456800	H	-3.76801800	-0.53902500	-1.84816000
H	-0.14771500	0.76614400	-2.03488600	H	-4.77158100	-0.89338500	-0.42702200
C	0.78938700	2.23799800	-0.76295600	H	-3.84024900	0.61546200	-0.49947400
H	1.70651600	2.35248600	-0.17208300	O	-0.30214300	-2.02833100	0.66945500
H	0.82131100	3.00616300	-1.54733000	H	1.31380600	-2.20205300	0.90536200

Conia-ene uncatalyzed product

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.254488 (Hartree/Particle)
Thermal correction to Energy= 0.269537

Thermal correction to Enthalpy= 0.270481
Thermal correction to Gibbs Free Energy= 0.211368
Sum of electronic and zero-point Energies= -654.212956
Sum of electronic and thermal Energies= -654.197907
Sum of electronic and thermal Enthalpies= -654.196963
Sum of electronic and thermal Free Energies= -654.256076

C	-1.05071600	2.57404900	-0.78201800	C	-1.67361500	-2.14471800	0.16999400
H	-0.51568000	3.12909400	-0.00476000	H	-0.98849100	-3.00423600	0.19795300
H	-1.90325100	3.16248800	-1.12759600	H	-2.61608300	-2.46889200	0.62320900
H	-0.34623900	2.41075000	-1.60551000	C	-1.05589400	-0.97437100	0.91924500
C	-1.55572600	1.26848900	-0.19283100	C	-0.94278900	-0.85237600	2.24073000
C	-0.56333100	0.07391600	-0.10188500	H	-1.32700900	-1.61736400	2.91096900
C	0.82465700	0.55109400	0.30903300	C	3.16088200	0.16495200	0.19211000
O	-2.71850700	1.12860600	0.12691900	H	3.34381800	1.22473600	-0.01026400
O	1.82030300	-0.16628200	-0.24577100	H	3.21864600	0.01946200	1.27541800
C	-0.65093000	-0.68729000	-1.46292000	C	4.12068200	-0.73723300	-0.55969500
H	-0.76919100	-0.01135100	-2.31728700	H	4.04141600	-0.58055800	-1.64031200
H	0.27666200	-1.24658800	-1.61304500	H	5.14986400	-0.51850900	-0.25496500
C	-1.83692400	-1.64783200	-1.27719500	H	3.91555300	-1.79133300	-0.34734000
H	-2.78181400	-1.10450900	-1.38023100	O	1.01724700	1.45129800	1.10384300
H	-1.83225100	-2.45841600	-2.01304900	H	-0.47606300	0.01417200	2.69948100

Diethyl zinc addition Pro-S TS

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.602166 (Hartree/Particle)
Thermal correction to Energy= 0.642283
Thermal correction to Enthalpy= 0.643227
Thermal correction to Gibbs Free Energy= 0.524353
Sum of electronic and zero-point Energies= -5099.338078
Sum of electronic and thermal Energies= -5099.297960
Sum of electronic and thermal Enthalpies= -5099.297016
Sum of electronic and thermal Free Energies= -5099.415891

C	-1.08988700	3.80132100	-0.36673300	C	0.01078300	-2.24737700	2.27208500
C	-1.52934000	2.59230200	0.21499200	C	-2.11684000	-2.44072000	3.40160700
C	-2.88435800	2.20881200	0.02654900	H	-3.76604500	-1.46722000	2.41986300
C	-3.74461100	3.05268800	-0.67971900	C	-0.75130100	-2.72778100	3.33369600
C	-3.29695400	4.24952100	-1.24515700	H	1.07394800	-2.45915800	2.20482400
C	-1.95814100	4.61444400	-1.09032800	H	-2.72109800	-2.81263500	4.22558100
H	-0.04978700	4.08529600	-0.22183900	H	-0.27667600	-3.32637500	4.10879300
H	-4.78518900	2.76011100	-0.77697700	O	-3.73292400	-1.23229200	-0.26758300
H	-3.98555400	4.88493800	-1.79725400	O	-4.76642200	0.67406800	0.37212200
H	-1.58862300	5.54116100	-1.52659800	H	-3.30780700	1.01638100	1.75966100
C	-3.38223000	0.92199000	0.67039600	O	-0.73094900	1.84661000	0.97157500
C	-2.65497400	-0.40347500	0.22228100	O	0.19494500	-1.01644600	0.23287800
H	-1.95687600	-0.19734400	-0.59167800	C	-4.85282600	-0.41377200	-0.54563900
C	-1.95463500	-1.18156300	1.31551100	C	-6.11910000	-1.20128100	-0.22467200
C	-0.57108300	-1.46836700	1.25136600	H	-6.18904600	-2.08352200	-0.86874400
C	-2.69944400	-1.67728200	2.39167800	H	-6.09173900	-1.52436000	0.81935800

H	-7.00511500	-0.57743700	-0.38249600
C	-4.82191900	0.06275500	-2.00531900
H	-5.67358200	0.71923900	-2.21623100
H	-3.90241600	0.61569900	-2.21137500
H	-4.86573100	-0.80120500	-2.67702800
Zn	0.75829100	0.82081000	0.42986600
O	1.94790500	1.20831300	-1.12913100
C	2.36606700	1.10273400	1.90405700
H	3.28084300	0.50913400	1.93021600
H	1.61069300	0.47802900	2.42080600
C	2.49259600	2.42085100	2.65425800
H	1.56085300	2.99661800	2.59584200
H	2.72337900	2.27970400	3.72187500
H	3.29480600	3.04988500	2.24485500
Zn	1.10413000	-2.20416200	-1.29260900
C	-0.01785900	-1.89845200	-2.88738500
H	0.57546100	-2.12146300	-3.78903900
H	-0.24386200	-0.82361600	-2.95531900
C	2.65387800	-3.10657600	-0.44574100
H	3.51085300	-3.10157100	-1.14003200
H	2.99922700	-2.54121700	0.43321000
C	2.38974700	-4.56382500	-0.02406700
H	2.08986700	-5.18769700	-0.87807200
H	3.26892300	-5.05383700	0.42894100
H	1.57775100	-4.63251400	0.71249500
C	-1.33861600	-2.68626000	-2.96167000
H	-2.00455100	-2.45154000	-2.12183000
H	-1.90981100	-2.47956100	-3.88332200
H	-1.17135700	-3.77317500	-2.93888600
C	2.76795700	1.72965900	-0.27364600
H	2.59732800	2.76764900	0.05319700
C	4.20842900	1.35261200	-0.31457700
C	4.60065000	0.10304600	-0.81618700
C	5.19201300	2.25927500	0.10274500
C	5.94965100	-0.23474600	-0.88267700
H	3.83780600	-0.59502900	-1.14354100
C	6.54429900	1.92246700	0.03288100
H	4.89465100	3.23841100	0.47072600
C	6.92592400	0.67259000	-0.45798500
H	6.24069800	-1.20979700	-1.26499200
H	7.29843300	2.63653100	0.35551200
H	7.97900600	0.40647400	-0.51272400

Diethyl zinc addition Pro-S precomlpex

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.601976 (Hartree/Particle)
Thermal correction to Energy= 0.643622
Thermal correction to Enthalpy= 0.644566
Thermal correction to Gibbs Free Energy= 0.520910
Sum of electronic and zero-point Energies= -5099.373462
Sum of electronic and thermal Energies= -5099.331816
Sum of electronic and thermal Enthalpies= -5099.330872
Sum of electronic and thermal Free Energies= -5099.454528

C	-0.83370900	2.33660200	3.00518500
C	-1.44812400	1.41481100	2.11917100
C	-2.23562400	1.94513000	1.05587500
C	-2.39436700	3.32524000	0.92768900
C	-1.77215800	4.22058300	1.80500300
C	-0.99089900	3.71294800	2.84659300
H	-0.24485300	1.93368400	3.82672100
H	-3.02520200	3.69671100	0.12577900
H	-1.90905200	5.29268600	1.68331500
H	-0.50969000	4.39184600	3.54999200
C	-2.94686400	0.96332500	0.13838000
C	-2.02137600	-0.05801400	-0.62382800
H	-0.97201800	0.20280300	-0.47900100
C	-2.23204300	-1.52016900	-0.30196400
C	-1.18703900	-2.33439100	0.19852800
C	-3.48265400	-2.09691100	-0.55249000
C	-1.45212100	-3.70236700	0.42284100
C	-3.73574400	-3.44698700	-0.31975700
H	-4.26888400	-1.46341700	-0.95718500
C	-2.70449300	-4.25288100	0.17008100
H	-0.63914900	-4.31334500	0.80705000
H	-4.71872300	-3.86488800	-0.52421500
H	-2.87563200	-5.31182700	0.35577800
O	-2.38122000	0.14046100	-2.01145800
O	-3.67101300	1.63445900	-0.90721500
H	-3.68482000	0.40295600	0.72371200
O	-1.33781800	0.11109100	2.26139900
O	0.04291200	-1.85625900	0.46496900
C	-3.01123100	1.39639200	-2.14838100
C	-4.07433500	1.28919400	-3.23725700
H	-3.60892800	1.04702400	-4.19794500
H	-4.78171900	0.49791700	-2.97587100
H	-4.61663100	2.23563300	-3.33503800
C	-1.97795500	2.49173000	-2.45752700
H	-2.46428100	3.47050500	-2.53856800
H	-1.22729200	2.54759300	-1.66517700
H	-1.47095300	2.26812700	-3.40238200
Zn	0.33182300	-0.86837600	2.17038900
O	1.52518100	0.54929200	0.81962200
C	1.52177700	-1.41302100	3.64937700

H	2.15199400	-2.24662100	3.30903500
H	0.91194100	-1.82275200	4.46916400
C	2.42961300	-0.30726400	4.21014600
H	1.84998800	0.53071800	4.62365200
H	3.09470500	-0.65763400	5.01827700
H	3.07781600	0.11467300	3.43004000
Zn	1.63871500	-1.90063500	-0.87693400
C	0.93703200	-1.59683500	-2.71271200
H	1.68036800	-1.05594100	-3.32223300
H	0.04845800	-0.95150000	-2.69804500
C	3.25298100	-2.40160600	0.16548900
H	3.37696300	-1.71434000	1.01505500
H	3.07469000	-3.38416300	0.63186200
C	4.57701400	-2.46698300	-0.61419200
H	4.83831300	-1.49593400	-1.06088800
H	5.44094000	-2.76394400	0.00648400
H	4.52820400	-3.18455000	-1.44582100
C	0.57368200	-2.90330100	-3.44290600
H	-0.20809200	-3.45720900	-2.90680100
H	0.19572600	-2.73867200	-4.46689200
H	1.43605500	-3.58056400	-3.53259100
C	1.69020000	1.74315900	0.59141000
H	1.24185300	2.49868500	1.25952500
C	2.46914200	2.24570500	-0.55157500
C	3.04046600	1.35523100	-1.47648600
C	2.63650900	3.62933300	-0.70755800
C	3.77837800	1.85631600	-2.54333800
H	2.87861400	0.28816000	-1.35586800
C	3.38003700	4.12555400	-1.77623500
H	2.17715000	4.30639800	0.00919000
C	3.95156100	3.23743800	-2.69122300
H	4.21491100	1.17177800	-3.26485200
H	3.51095000	5.19724800	-1.89972100
H	4.52986000	3.62238300	-3.52775300

Diethyl zinc addition Pro-S product

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.605872 (Hartree/Particle)
Thermal correction to Energy= 0.646061
Thermal correction to Enthalpy= 0.647005
Thermal correction to Gibbs Free Energy= 0.525733
Sum of electronic and zero-point Energies= -5099.401193
Sum of electronic and thermal Energies= -5099.361004
Sum of electronic and thermal Enthalpies= -5099.360060
Sum of electronic and thermal Free Energies= -5099.481332

C	0.68868600	3.75809700	-0.66282700
C	1.37903500	2.53474200	-0.79051300
C	2.70893400	2.45495200	-0.30204000
C	3.30337100	3.59006700	0.25529300
C	2.60918700	4.79625700	0.37465200
C	1.29273900	4.87152600	-0.08384600
H	-0.32950600	3.80996000	-1.04134400
H	4.33154900	3.51537000	0.59462800
H	3.09233400	5.66339400	0.81857200
H	0.73479400	5.80243900	0.00058500
C	3.49258500	1.16025600	-0.47654400
C	2.83003000	-0.14185600	0.11023400
H	1.91380600	0.11058800	0.64958800
C	2.55527400	-1.24788000	-0.88521100
C	1.26776700	-1.81185400	-1.04315700
C	3.62004400	-1.76976800	-1.62959500
C	1.10300800	-2.88239100	-1.94565000
C	3.44930700	-2.82437100	-2.52302600
H	4.60891500	-1.34049900	-1.48400400
C	2.17710300	-3.38312600	-2.67390100
H	0.10637500	-3.29823200	-2.05981100
H	4.29579700	-3.20936000	-3.08636400
H	2.01901700	-4.21002900	-3.36356000
O	3.80994700	-0.63154300	1.04832700
O	4.77277000	1.21745600	0.17163600
H	3.68949400	1.00786000	-1.54355000
O	0.83134300	1.48228200	-1.40652200
O	0.20053200	-1.36969700	-0.34679000
C	4.72785700	0.40409600	1.34342200
C	6.10792500	-0.21362000	1.54183000
H	6.09543300	-0.89769400	2.39612200
H	6.39002600	-0.77127400	0.64502900
H	6.85208400	0.56823300	1.72613800
C	4.26686400	1.19823100	2.57460500
H	4.96465300	2.01447200	2.79213500
H	3.27645400	1.62937000	2.40952100
H	4.21662800	0.53408000	3.44401600
Zn	-0.43053200	0.41880200	-0.53609500
O	-2.09298500	0.62272900	0.19824600
C	-3.01528600	1.60521300	-1.82069200
H	-3.32853800	0.60832500	-2.15971800
H	-1.97485000	1.74207500	-2.15169400
C	-3.89094100	2.68299800	-2.46563500
H	-3.58832300	3.68732100	-2.14136800
H	-3.81004200	2.65153200	-3.55883000
H	-4.94613300	2.55325700	-2.20132700
Zn	-1.22485300	-2.51881300	0.81231100
C	-0.57697300	-2.24788100	2.65405500

H	-1.27043900	-2.73733800	3.35667500
H	-0.64871600	-1.17536900	2.89350500
C	-2.45331200	-3.35200000	-0.49545200
H	-3.49248900	-3.15676700	-0.18416100
H	-2.35686400	-2.86012100	-1.47548500
C	-2.28691800	-4.87069800	-0.68265200
H	-2.43038300	-5.41580000	0.26110600
H	-2.99836400	-5.30362800	-1.40685300
H	-1.28059800	-5.13107600	-1.04032500
C	0.85338900	-2.72687900	2.95754800
H	1.59775900	-2.22814600	2.32443700
H	1.15455400	-2.54431800	4.00345300
H	0.96951200	-3.80672600	2.78542300
C	-2.99061700	1.58783900	-0.26965900
H	-2.69293700	2.60412900	0.05864800
C	-4.38091300	1.32060400	0.30103100
C	-4.86059800	0.00682600	0.39605600
C	-5.21263800	2.36534200	0.71987100
C	-6.14088900	-0.25032600	0.88485200
H	-4.20852400	-0.80918900	0.10071700
C	-6.49677000	2.11267800	1.21016400
H	-4.84602100	3.38919000	0.67140900
C	-6.96667400	0.80166100	1.29217700
H	-6.49345400	-1.27703900	0.95492900
H	-7.12447100	2.93991000	1.53538800
H	-7.96332300	0.59921900	1.67839200

Diethyl zinc addition Pro-R TS

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.602334 (Hartree/Particle)
Thermal correction to Energy= 0.642187
Thermal correction to Enthalpy= 0.643131
Thermal correction to Gibbs Free Energy= 0.526450
Sum of electronic and zero-point Energies= -5099.340015
Sum of electronic and thermal Energies= -5099.300161
Sum of electronic and thermal Enthalpies= -5099.299217
Sum of electronic and thermal Free Energies= -5099.415899

C	0.15352600	3.49898200	0.11964200
C	-0.69648500	2.45395000	0.54023000
C	-2.07004200	2.51381700	0.18706700
C	-2.54350000	3.62509400	-0.51554200
C	-1.69349900	4.65720400	-0.92055900
C	-0.33588100	4.58268100	-0.60498600
H	1.20413100	3.43980500	0.39506700
H	-3.60405900	3.67536200	-0.73825900
H	-2.08946400	5.50564400	-1.47371800
H	0.34398800	5.37525200	-0.91351700
C	-3.01457400	1.41187600	0.65477800
C	-2.69862900	-0.04697300	0.14292100
H	-1.86818800	-0.03073500	-0.56610300
C	-2.44611700	-1.09603600	1.20607900
C	-1.23073900	-1.82171600	1.25732700
C	-3.46191300	-1.40834200	2.11720400
C	-1.10075000	-2.85595900	2.20835200
C	-3.31577400	-2.41591700	3.06866000
H	-4.39532400	-0.85333300	2.05770500
C	-2.12540900	-3.14818600	3.10278200
H	-0.16863200	-3.41485600	2.21786100
H	-4.12267500	-2.63575800	3.76372900
H	-1.99502200	-3.94905000	3.82857800
O	-3.90840100	-0.43229900	-0.54836600
O	-4.36213500	1.64712400	0.21538900
H	-3.03781600	1.40653100	1.75019800
O	-0.24643700	1.45935400	1.30458500
O	-0.20585700	-1.55291900	0.42953300
C	-4.67748400	0.72065500	-0.82357700
C	-6.15501400	0.36143600	-0.69787200
H	-6.42177200	-0.40118700	-1.43627800
H	-6.35174500	-0.02954900	0.30384600
H	-6.77748900	1.24702400	-0.86407800
C	-4.33596100	1.27270500	-2.21570000
H	-4.91220700	2.18078500	-2.42680800
H	-3.27281800	1.51375200	-2.28692000
H	-4.57045500	0.51994800	-2.97577200
Zn	0.83069100	0.01564800	0.80156300
O	1.97079900	-0.23576500	-0.84475900
C	2.51256300	-0.10981300	2.19968600
H	3.40846100	-0.72520200	2.29188200
H	1.74600600	-0.66658300	2.77126800
C	2.72612500	1.27844300	2.79581600
H	1.79641100	1.85523500	2.80558100
H	3.09859800	1.22102000	3.83108100
H	3.46571200	1.85070300	2.22253200
Zn	0.77380100	-2.22257100	-1.46321300
C	-0.30218200	-1.46078100	-2.94255600
H	0.30129700	-1.50297700	-3.86510300
H	-0.44854900	-0.38444800	-2.75986700
C	1.98570600	-3.66789100	-0.82563700
H	2.30373100	-3.48277500	0.21395700

H	1.39373200	-4.59604400	-0.75981300
C	3.23129300	-3.95342900	-1.68149700
H	3.89317000	-3.07726300	-1.74792100
H	3.85184100	-4.78536800	-1.30243100
H	2.96168300	-4.21026700	-2.71562300
C	-1.67212400	-2.10053400	-3.22752700
H	-2.35606200	-1.99559200	-2.37555800
H	-2.18749700	-1.65451600	-4.09697500
H	-1.58837300	-3.17734900	-3.43634800
C	2.96848600	-0.39386700	-0.01509100
H	3.25105400	-1.42246500	0.23146300
C	4.10563600	0.56229400	-0.07601600
C	5.35959100	0.21212500	0.44389100
C	3.95124400	1.80730600	-0.70274300
C	6.43710300	1.09136200	0.35211500
H	5.48895800	-0.75954800	0.91561300
C	5.02829100	2.68731500	-0.79335500
H	2.98402600	2.06038100	-1.12534400
C	6.27320800	2.33393400	-0.26551200
H	7.40563900	0.80580700	0.75553900
H	4.89817200	3.64997200	-1.28165500
H	7.11283700	3.02095600	-0.33966500

Diethyl zinc addition Pro-R precomplex

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.606128 (Hartree/Particle)
Thermal correction to Energy= 0.645979
Thermal correction to Enthalpy= 0.646924
Thermal correction to Gibbs Free Energy= 0.528469
Sum of electronic and zero-point Energies= -5099.407495
Sum of electronic and thermal Energies= -5099.367644
Sum of electronic and thermal Enthalpies= -5099.366700
Sum of electronic and thermal Free Energies= -5099.485154

C	-1.12753600	-2.79548200	-1.77436600
C	-1.65372200	-1.52759200	-1.43832700
C	-3.06601800	-1.38895600	-1.34766200
C	-3.88122400	-2.48370600	-1.64417800
C	-3.34643200	-3.72983300	-1.98329700
C	-1.95986000	-3.88041400	-2.03899400
H	-0.04589700	-2.89086300	-1.83932200
H	-4.95693400	-2.34386000	-1.61292100
H	-4.00577200	-4.56643900	-2.20290200
H	-1.52231500	-4.84298000	-2.29955000
C	-3.65955700	-0.02504100	-1.01664000
C	-3.24145900	0.60658400	0.36708200
H	-2.63764900	-0.10053100	0.94131300
C	-2.53908200	1.94534200	0.30568400
C	-1.23539800	2.12445900	0.84521000
C	-3.21265900	3.04149100	-0.24437300
C	-0.68804800	3.43047900	0.81956700
C	-2.65065000	4.31639700	-0.27959000
H	-4.21469400	2.88431600	-0.63839700
C	-1.37714500	4.50415200	0.26642100
H	0.30056100	3.56390600	1.25256800
H	-3.19914100	5.14880500	-0.71417500
H	-0.91953000	5.49248700	0.26168200
O	-4.50651300	0.80545500	1.04298800
O	-5.09551700	-0.07044500	-0.95847300
H	-3.40101000	0.67774500	-1.81612600
O	-0.86599400	-0.47561700	-1.25423200
O	-0.54079000	1.13165800	1.39759500
C	-5.50445700	0.03945100	0.40255700
C	-6.81616200	0.81905600	0.43750100
H	-7.13474700	0.97811500	1.47272900
H	-6.67473500	1.79058000	-0.04308200
H	-7.60085700	0.26902700	-0.09271000
C	-5.63565000	-1.33714800	1.07414800
H	-6.39287000	-1.94733100	0.56898800
H	-4.68397600	-1.87290300	1.03965900
H	-5.92755100	-1.20949300	2.12253200
Zn	0.25877200	-0.14306000	0.23276400
O	2.19095500	0.01055000	-0.09716600
C	2.19478300	1.91684700	-1.62908400
H	2.80977100	2.78973700	-1.89233800
H	1.27025500	2.31537600	-1.18942900
C	1.85917900	1.11255400	-2.88834600
H	1.16434200	0.29937000	-2.66032800
H	1.37807900	1.75909300	-3.63203900
H	2.76072600	0.68705400	-3.34501000
Zn	2.29745400	-0.85236400	1.70934100
C	0.57808200	-1.98056300	1.68686700
H	1.11810500	-2.94247000	1.64086600
H	-0.18077800	-2.14897100	0.90266300
C	3.84303200	-0.57910000	2.89871500
H	4.23432800	0.43699100	2.74112800
H	3.50979100	-0.60223400	3.94671700
C	4.99315800	-1.58517500	2.71584500
H	5.38603800	-1.57030500	1.69100800
H	5.84622500	-1.38582700	3.38532500
H	4.67140200	-2.61656600	2.91841000
C	-0.15808700	-1.87342000	3.03520800

H	-0.72985100	-0.94089500	3.09157900
H	-0.85862800	-2.70553500	3.20269300
H	0.54468800	-1.86845000	3.87896700
C	2.93703200	1.12806600	-0.52261300
H	3.07480700	1.83145400	0.31798500
C	4.33400100	0.70858600	-0.97757500
C	5.37925500	1.64233800	-0.99589500
C	4.60221500	-0.59695800	-1.40579000
C	6.65469800	1.28770300	-1.43532600
H	5.19147400	2.65840900	-0.65273200
C	5.87829200	-0.95718000	-1.84566500
H	3.79668300	-1.32355100	-1.38309700
C	6.90988300	-0.01711800	-1.86384500
H	7.45223400	2.02770600	-1.43514100
H	6.06622600	-1.97723000	-2.17383300
H	7.90450400	-0.29873500	-2.20197500

Diethyl zinc addition Pro-R product

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.601454 (Hartree/Particle)
Thermal correction to Energy= 0.643241
Thermal correction to Enthalpy= 0.644185
Thermal correction to Gibbs Free Energy= 0.519465
Sum of electronic and zero-point Energies= -5099.371380
Sum of electronic and thermal Energies= -5099.329593
Sum of electronic and thermal Enthalpies= -5099.328649
Sum of electronic and thermal Free Energies= -5099.453368

C	2.55890500	1.09762000	2.49529600
C	1.34179900	1.48583000	1.88208100
C	1.38306600	2.56171700	0.94774100
C	2.59376600	3.19903200	0.67464900
C	3.78829000	2.79900900	1.28461700
C	3.75855400	1.74502600	2.20189900
H	2.52577600	0.28723200	3.21945400
H	2.58842800	4.03004700	-0.02416100
H	4.71865500	3.31597000	1.06006600
H	4.67334700	1.42914000	2.70236300
C	0.07291100	3.05592900	0.35307400
C	-0.82886700	1.97623600	-0.35482900
H	-0.29586900	1.02889000	-0.44368400
C	-2.18680000	1.74618500	0.26973000
C	-2.59843400	0.46774200	0.71777500
C	-3.07890600	2.82051600	0.36841000
C	-3.89753000	0.32928600	1.25177000
C	-4.35715400	2.67463700	0.90317700
H	-2.75664400	3.79135700	-0.00186400
C	-4.76461600	1.41300300	1.34548000
H	-4.19618400	-0.65967400	1.59004100
H	-5.02706900	3.52901700	0.96654700
H	-5.76020400	1.27266400	1.76304300
O	-1.04000600	2.53622100	-1.67274600
O	0.28749600	4.05652000	-0.65706700
H	-0.51134400	3.53576000	1.14696400
O	0.18834000	0.91479600	2.16726700
O	-1.80839900	-0.61712300	0.63781300
C	-0.03080200	3.48986100	-1.92747700
C	-0.61615800	4.59129900	-2.80486000
H	-0.92520400	4.17991800	-3.77100400
H	-1.48810100	5.02544600	-2.30867600
H	0.12641300	5.37778300	-2.97636000
C	1.19746000	2.82735200	-2.57073200
H	1.98580100	3.56694300	-2.75108800
H	1.60147600	2.05014400	-1.91723700
H	0.91506700	2.36863400	-3.52440600
Zn	-0.32278400	-0.91731800	1.87768300
O	0.56658000	-1.76015600	-0.29265800
C	0.08005000	-2.53474100	2.92778600
H	0.36837500	-3.34388300	2.24247600
H	-0.85619600	-2.87986100	3.39189700
C	1.15118500	-2.39232000	4.01970800
H	0.89349200	-1.60869100	4.74478400
H	1.30617700	-3.32056100	4.59638900
H	2.12819100	-2.11796500	3.59887900
Zn	-1.86315200	-2.04250100	-0.91545500
C	-1.65324300	-1.15934000	-2.68732200
H	-0.71105100	-1.50864200	-3.14770100
H	-1.52142100	-0.07466800	-2.56964600
C	-2.36288700	-3.75167300	-0.02575100
H	-1.89270600	-3.79883600	0.96760800
H	-3.44600000	-3.73328300	0.18236100
C	-2.03963300	-5.05065100	-0.78304300
H	-0.95943500	-5.15831100	-0.96503700
H	-2.35344600	-5.96636400	-0.25005300
H	-2.52240500	-5.08184500	-1.77033700
C	-2.79572800	-1.40570700	-3.68697500
H	-3.75327200	-1.02473000	-3.30544300
H	-2.63665400	-0.92066900	-4.66663000
H	-2.94566900	-2.47676200	-3.88742500
C	1.34985800	-2.32428900	-1.04732400
H	0.98482200	-3.15344500	-1.68233600
C	2.77121000	-1.98530100	-1.20341900

C	3.56125900	-2.75901000	-2.06812600
C	3.33868300	-0.89691900	-0.52047500
C	4.90865500	-2.45515300	-2.24492800
H	3.11127900	-3.59593100	-2.59812700
C	4.68413500	-0.59270200	-0.70362000
H	2.72641300	-0.29558800	0.14358300
C	5.46801000	-1.37051200	-1.56260500
H	5.52048700	-3.05560100	-2.91297000
H	5.10974700	0.25552900	-0.17625700
H	6.51870500	-1.12844900	-1.70397700

Diethyl zinc addition with Ti Pro-R TS

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.971871 (Hartree/Particle)
Thermal correction to Energy= 1.033032
Thermal correction to Enthalpy= 1.033976
Thermal correction to Gibbs Free Energy= 0.873483
Sum of electronic and zero-point Energies= -4050.230268
Sum of electronic and thermal Energies= -4050.169107
Sum of electronic and thermal Enthalpies= -4050.168162
Sum of electronic and thermal Free Energies= -4050.328656

C	-2.74026700	1.65127800	2.72695800
C	-2.77253100	0.74348600	1.65538000
C	-3.92425200	0.64756100	0.84228200
C	-5.02635100	1.44963300	1.15574600
C	-4.99619000	2.35057200	2.22116700
C	-3.84585600	2.45087800	3.00558600
H	-1.83949700	1.69871600	3.32918500
H	-5.91819500	1.35338900	0.54587800
H	-5.86645100	2.96401900	2.43795500
H	-3.80892900	3.14705500	3.84006200
C	-4.00484200	-0.37715800	-0.28547200
C	-2.79578700	-0.39963800	-1.28999200
H	-2.06873700	0.35990800	-1.01028400
C	-2.10647900	-1.74138100	-1.43011200
C	-0.75792200	-1.94903400	-1.07228500
C	-2.83535700	-2.81850400	-1.95522900
C	-0.19258700	-3.22610300	-1.23432500
C	-2.27085200	-4.07920100	-2.11935600
H	-3.86780300	-2.64630100	-2.24609300
C	-0.93698500	-4.27964600	-1.75432600
H	0.83701200	-3.36953900	-0.93270000
H	-2.86140600	-4.89434800	-2.52843800
H	-0.47700500	-5.25837600	-1.86873300
O	-3.38874300	-0.05779400	-2.55474600
O	-5.14206300	-0.16123500	-1.12575500
H	-4.13049800	-1.37378900	0.15247400
O	-1.71986100	-0.04951700	1.40454700
O	-0.00388300	-0.93774300	-0.54558700
C	-4.70425300	0.43973600	-2.34408000
C	-5.60492100	-0.05812800	-3.46732500
H	-5.25555000	0.32754900	-4.42983400
H	-5.58982500	-1.15050600	-3.49660700
H	-6.63362400	0.27874000	-3.30588000
C	-4.68354200	1.97187000	-2.25485100
H	-5.68818900	2.36184500	-2.06107800
H	-4.02627900	2.30656700	-1.44800300
H	-4.32191500	2.39009000	-3.20032700
Ti	0.01630000	-0.68097400	1.54497100
Ti	2.01182700	-0.22120200	-0.82783900
O	-0.28691300	-2.35864400	2.10554400
O	0.92814600	1.21744700	0.48449800
C	0.37771700	1.90360900	-0.44349700
H	-0.54592600	1.53775900	-0.89131400
C	-0.83354600	-2.98342000	3.26227700
H	-0.61035200	-2.33793100	4.12576800
C	-0.15250900	-4.33723200	3.46419800
H	-0.34703600	-4.99310400	2.60806100
H	0.93066400	-4.21504400	3.56716200
H	-0.53223700	-4.82622600	4.36906600
C	-2.35027100	-3.11055500	3.11392100
H	-2.59665400	-3.74484000	2.25491800
H	-2.78658600	-3.55881700	4.01470700
H	-2.80493400	-2.12799000	2.95964800
C	0.65221100	3.34370100	-0.57648500
C	1.65722300	3.95987900	0.18725000
C	-0.13996500	4.12324200	-1.43507200
C	1.87044500	5.33146100	0.08313100
H	2.24907400	3.34964700	0.86067000
C	0.07739800	5.49520100	-1.53837100
H	-0.92742700	3.65050100	-2.01596600
C	1.08380400	6.10007900	-0.78120300
H	2.64545700	5.80602300	0.67866300
H	-0.54032800	6.09325500	-2.20216500
H	1.25065600	7.17108400	-0.85827200
O	2.03298800	-0.98803800	1.01853000
O	2.49805700	-1.58764200	-1.85444500
O	0.50780700	0.11585800	3.08971800
C	1.24082300	1.12028300	-2.57809600

H	2.08483200	0.55324400	-2.99835200
H	1.53322200	2.16898700	-2.64702000
C	-0.02125100	0.80945800	-3.37000300
H	-0.28155900	-0.25215800	-3.33301900
H	-0.90194400	1.35742200	-3.01582900
H	0.10396400	1.07813400	-4.43014100
C	1.49636200	0.89850100	3.72960800
H	2.37357900	0.93787700	3.06770000
C	1.89253900	0.22987800	5.04925700
H	2.25220000	-0.78960200	4.87710700
H	2.68721000	0.79708900	5.54860000
H	1.02890300	0.17862300	5.72230400
C	0.98552000	2.32475000	3.94747300
H	0.68286100	2.77435800	2.99748200
H	0.12302100	2.32631400	4.62412700
H	1.76947800	2.94838500	4.39446800
C	2.94669100	-1.82613100	1.73930500
H	2.55370500	-1.88371700	2.76251400
C	4.33995000	-1.19963100	1.79232000
H	4.99970600	-1.80516600	2.42542800
H	4.78137100	-1.14000600	0.79228900
H	4.29789200	-0.18717900	2.20448700
C	2.97628100	-3.24158300	1.16156400
H	1.96760400	-3.66090400	1.13693200
H	3.38395200	-3.23662500	0.14554900
H	3.60803200	-3.89076800	1.78036400
C	3.00229800	-2.59038500	-2.71335500
H	2.78397100	-3.55996800	-2.24036000
C	4.51835300	-2.44814000	-2.85937400
H	5.00734500	-2.47868800	-1.88011200
H	4.91954400	-3.26476800	-3.47093100
H	4.77263300	-1.49786900	-3.34094200
C	2.27117600	-2.53231100	-4.05585600
H	2.46250200	-1.57768300	-4.55946900
H	2.61504200	-3.34126100	-4.71087900
H	1.19321800	-2.63923800	-3.90650000
C	4.37139700	1.85357300	-1.12116200
H	3.76995500	2.73936800	-1.37436200
C	5.22119100	2.17778000	0.10978400
H	5.85012000	1.32281600	0.38019700
H	5.87182100	3.03677700	-0.09136600
H	4.58461700	2.41767100	0.96729000
C	5.23077600	1.48171600	-2.33182600
H	5.83566300	0.59438100	-2.11459400
H	4.60271800	1.26852100	-3.20277900
H	5.90575800	2.30641100	-2.58939500
O	3.47408300	0.80582000	-0.81724800

Diethyl zinc addition with Ti Pro-R precomplex

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.971693 (Hartree/Particle)
Thermal correction to Energy= 1.034000
Thermal correction to Enthalpy= 1.034944
Thermal correction to Gibbs Free Energy= 0.870448
Sum of electronic and zero-point Energies= -4050.255167
Sum of electronic and thermal Energies= -4050.192859
Sum of electronic and thermal Enthalpies= -4050.191915
Sum of electronic and thermal Free Energies= -4050.356411

C	-3.46829500	0.85784300	1.93535700
C	-2.92583500	-0.23981800	1.24422100
C	-3.72839000	-0.94664800	0.32019500
C	-5.05970900	-0.55384600	0.15297800
C	-5.59884800	0.53038900	0.84759300
C	-4.79462500	1.23891100	1.73931900
H	-2.82718000	1.38974000	2.62781300
H	-5.67395000	-1.12055100	-0.53822000
H	-6.63683700	0.81275000	0.69412600
H	-5.19770600	2.08523200	2.29102000
C	-3.18758000	-2.16697200	-0.41144100
C	-1.82308800	-1.97250400	-1.16862500
H	-1.50000700	-0.93151200	-1.12251800
C	-0.71854100	-2.88407600	-0.68220400
C	0.47379100	-2.39279300	-0.12091300
C	-0.88645600	-4.27261300	-0.79543800
C	1.45088600	-3.30029100	0.32812800
C	0.08226300	-5.16851900	-0.35625200
H	-1.80051600	-4.64407200	-1.25052000
C	1.26043900	-4.67352900	0.21147600
H	2.35894500	-2.89757100	0.76241500
H	-0.07556300	-6.23876000	-0.45760400
H	2.02991800	-5.35660500	0.56370400
O	-2.13417800	-2.32881900	-2.52728200
O	-4.08659400	-2.62541700	-1.42483300
H	-3.08656700	-2.98771600	0.30805300
O	-1.65689900	-0.63250000	1.46992100
O	0.70866800	-1.05454800	0.01061000
C	-3.54084500	-2.29798800	-2.70467100
C	-3.93568400	-3.39657500	-3.68286800
H	-3.48143700	-3.21211200	-4.66107500
H	-3.59087100	-4.36359300	-3.30814100

H	-5.02340200	-3.42755700	-3.79992800
C	-3.99486600	-0.90923000	-3.17533700
H	-5.08467500	-0.87298500	-3.27632700
H	-3.69123400	-0.13714500	-2.46327800
H	-3.54413000	-0.68445800	-4.14776500
Ti	0.08219700	0.04676700	1.68428000
Ti	2.29334600	0.07055600	-0.86567600
O	0.72139000	-1.05995900	2.91598300
O	-0.68562800	1.48322400	0.03256900
C	-1.23495400	2.57120200	0.21293900
H	-1.29835900	2.96905500	1.23731100
C	0.65913000	-1.97623800	3.99878500
H	0.37533800	-1.39988200	4.89204900
C	2.04819500	-2.57388700	4.22668200
H	2.35938000	-3.15466700	3.35223700
H	2.78565100	-1.78298000	4.39980500
H	2.03965200	-3.23739500	5.09937400
C	-0.40799500	-3.03979200	3.73815500
H	-0.13618900	-3.65389400	2.87377200
H	-0.50994400	-3.69163800	4.61402600
H	-1.37539300	-2.57162100	3.53475100
C	-1.79832700	3.39272800	-0.86020500
C	-1.78797200	2.95853000	-2.19754700
C	-2.35710100	4.63815500	-0.53268300
C	-2.32800100	3.76809400	-3.19007300
H	-1.35849300	1.99102400	-2.43622500
C	-2.89520800	5.44741700	-1.53016100
H	-2.36667300	4.96492600	0.50450400
C	-2.87989200	5.01127500	-2.85726300
H	-2.32363000	3.43495500	-4.22379600
H	-3.32676300	6.41135900	-1.27702300
H	-3.30129500	5.64037700	-3.63674800
O	1.84557800	0.86486600	0.97734600
O	3.51754400	-1.20392000	-0.94997900
O	-0.26389100	1.48417000	2.80218700
C	1.13196900	-0.24795600	-2.61411400
H	0.25924300	0.40112500	-2.44229900
H	0.77193800	-1.28042500	-2.54588100
C	1.74141900	0.00385000	-3.99270000
H	1.98470900	1.05956700	-4.15356300
H	2.66603300	-0.56962700	-4.14036700
H	1.05495200	-0.29361200	-4.80034700
C	-0.08143400	1.72174400	4.19110700
H	0.81996900	1.17991200	4.51921600
C	-1.27158100	1.19582000	5.00049100
H	-1.46585200	0.14437400	4.77014000
H	-1.07106000	1.28595300	6.07510300
H	-2.18029400	1.76654700	4.77780600
C	0.13604200	3.21808300	4.43203700
H	1.00711700	3.58395600	3.88079600
H	-0.74278900	3.78627100	4.10352700
H	0.29360300	3.42003500	5.49828400
C	2.67886100	1.68902300	1.80949600
H	2.30667300	1.57457600	2.83362400
C	2.55553200	3.16001200	1.41553900
H	3.15988900	3.78875200	2.08147300
H	2.89661900	3.30922400	0.38887300
H	1.51398700	3.48569300	1.48837000
C	4.12628000	1.19115100	1.79186100
H	4.17055800	0.13441900	2.07615500
H	4.57271000	1.30689200	0.79966100
H	4.73024100	1.76385800	2.50626300
C	4.66667700	-1.99277200	-1.18792400
H	4.89133900	-2.52057500	-0.24821100
C	5.85966600	-1.10623800	-1.54734700
H	6.04449500	-0.36807600	-0.76031100
H	6.76400200	-1.71369900	-1.67025400
H	5.67157300	-0.57316100	-2.48623000
C	4.35760900	-3.02934500	-2.26929900
H	4.13671000	-2.53351300	-3.22128300
H	5.21540900	-3.69648000	-2.41609100
H	3.48985600	-3.63088500	-1.98430500
C	3.69876800	2.45036100	-2.41297400
H	3.89894500	1.90902400	-3.34909800
C	2.75832500	3.61897100	-2.72111500
H	2.55198100	4.19915500	-1.81477800
H	3.20633200	4.28913800	-3.46453800
H	1.80559300	3.25182100	-3.11526800
C	5.03838400	2.92391700	-1.84130200
H	4.89142300	3.49340700	-0.91697800
H	5.68746900	2.07066800	-1.62163800
H	5.55268400	3.56975200	-2.56289900
O	3.07524000	1.55003700	-1.52070400

Diethyl zinc addition with Ti Pro-R product

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.975021 (Hartree/Particle)
Thermal correction to Energy= 1.036751
Thermal correction to Enthalpy= 1.037696
Thermal correction to Gibbs Free Energy= 0.870603
Sum of electronic and zero-point Energies= -4050.313544
Sum of electronic and thermal Energies= -4050.251813
Sum of electronic and thermal Enthalpies= -4050.250869
Sum of electronic and thermal Free Energies= -4050.417961

C	4.08625800	-1.12561800	-1.92923300
C	3.52605400	-0.77842300	-0.68962300
C	4.12164600	0.23554100	0.09137000
C	5.25936600	0.88009400	-0.40709600
C	5.80601000	0.54508700	-1.64591300
C	5.21897200	-0.46883700	-2.40421400
H	3.61192600	-1.91057600	-2.50936100
H	5.71940400	1.64797200	0.20523800
H	6.69037000	1.06254100	-2.00738400
H	5.64166800	-0.75274000	-3.36487700
C	3.63751000	0.53031500	1.50481500
C	2.09379800	0.75300000	1.71064600
H	1.57407000	0.81383500	0.75295000
C	1.47284700	-0.31419400	2.58380400
C	0.51255600	-1.21556900	2.09574000
C	1.92342900	-0.46962100	3.90267900
C	0.08403700	-2.28448600	2.89944100
C	1.47646300	-1.50939600	4.71274800
H	2.64676800	0.24474800	4.28636200
C	0.56298600	-2.43362300	4.19800300
H	-0.63852600	-2.98118600	2.48499400
H	1.84649700	-1.60718200	5.72946800
H	0.21976300	-3.26600000	4.80730400
O	2.01637400	2.02327100	2.37854900
O	4.23373900	1.71089800	2.04920500
H	3.96126800	-0.29790500	2.14597500
O	2.42991800	-1.43041100	-0.23263800
O	-0.02840100	-1.08123100	0.84864700
C	3.23645500	2.72456500	2.16258300
C	3.54159400	3.55947400	3.39832800
H	2.75875300	4.30838000	3.55219600
H	3.59116600	2.91115000	4.27679800
H	4.50078100	4.07284600	3.28084500
C	3.16273300	3.57119700	0.88568200
H	4.12173200	4.06601300	0.70128900
H	2.92780200	2.94943100	0.01711200
H	2.38827400	4.33881400	0.98937600
Ti	0.69412100	-1.73331200	-0.85179200
Ti	-2.10970800	-0.31559000	0.29784500
O	0.73604500	-3.52165900	-1.00271900
O	-1.39440000	1.30067500	0.05981500
C	-1.19363500	2.69194500	0.21823800
H	-0.20747200	2.82835400	0.68545700
C	1.68220900	-4.58359000	-0.90629300
H	2.63359300	-4.15102400	-0.56451300
C	1.88098000	-5.21135700	-2.28574800
H	0.94141500	-5.64327800	-2.64947600
H	2.21556900	-4.45918600	-3.00790500
H	2.63388100	-6.00714800	-2.24245300
C	1.19222500	-5.58987600	0.13475400
H	0.23377900	-6.02416100	-0.17285000
H	1.91755400	-6.40311200	0.25532000
H	1.05720100	-5.10056100	1.10466300
C	-1.19631700	3.37542700	-1.14180700
C	-2.14368900	3.02413100	-2.11388000
C	-0.27511500	4.38782400	-1.43260900
C	-2.17014000	3.67830900	-3.34553500
H	-2.85038200	2.22719100	-1.90223700
C	-0.30359600	5.04788700	-2.66362000
H	0.47421200	4.65950100	-0.69278400
C	-1.25185100	4.69450800	-3.62389900
H	-2.90908100	3.39448500	-4.09081200
H	0.42037700	5.83118000	-2.87295000
H	-1.27391400	5.20358900	-4.58392600
O	-1.43761800	-1.55363200	-1.08518200
O	-2.58781700	-0.61107500	1.98553000
O	0.89434100	-0.92694500	-2.43050400
C	-2.25645300	3.26798800	1.17618200
H	-2.25633000	2.63784800	2.07305700
H	-3.24230400	3.15876400	0.70600200
C	-2.01673500	4.72784200	1.57123800
H	-1.04179900	4.85073100	2.05868200
H	-2.04451600	5.39317700	0.70204000
H	-2.78379200	5.06517300	2.27698100
C	0.58859700	0.05708100	-3.40827100
H	-0.44617200	0.38357200	-3.23530800
C	0.69286200	-0.57880500	-4.79516600
H	0.03059800	-1.44724300	-4.87474300
H	0.41284300	0.14303300	-5.57123300
H	1.72002300	-0.91026000	-4.98499500
C	1.51014300	1.26649700	-3.24856700
H	1.40868800	1.69693400	-2.24793100
H	2.55564500	0.98076900	-3.40087200
H	1.24185000	2.04190500	-3.97513800
C	-2.06169700	-2.38978400	-2.08753600
H	-1.23676800	-2.87124000	-2.62553400
C	-2.87929800	-1.57775100	-3.09023800
H	-3.28835500	-2.24590700	-3.85801400
H	-3.70258300	-1.05994900	-2.59475300
H	-2.25316500	-0.83232400	-3.58929100
C	-2.87552300	-3.48464600	-1.39934300
H	-2.23982100	-4.04443500	-0.70628800
H	-3.71485600	-3.05268100	-0.84466900
H	-3.27947100	-4.18575600	-2.13949800
C	-2.96733200	-0.84240400	3.33069000
H	-2.05568100	-1.11072300	3.87834900
C	-3.94267000	-2.01919100	3.39707600
H	-3.50295200	-2.90968100	2.93566300
H	-4.18509900	-2.25660100	4.43947200
H	-4.87507400	-1.78262000	2.87217300
C	-3.54558900	0.43379800	3.94353000
H	-4.46026600	0.73915900	3.42206400
H	-3.78942900	0.26979200	4.99969900
H	-2.82114400	1.25161200	3.88338300
C	-5.11083600	0.08628400	0.03799000
H	-5.08458100	0.33552400	1.10949100
C	-5.69692400	1.27366600	-0.72918000
H	-5.74830400	1.05014700	-1.80111900
H	-6.71007100	1.49931400	-0.37573300
H	-5.07893400	2.16688700	-0.59462200
C	-5.95068300	-1.17980900	-0.14450400
H	-5.99436700	-1.46592200	-1.20150500
H	-5.52291800	-2.01366900	0.42130300
H	-6.97565800	-1.01571500	0.20894300

O	-3.77851100	-0.14396900	-0.39228100

Diethyl zinc addition with Ti Pro-S TS

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.972279 (Hartree/Particle)
Thermal correction to Energy= 1.033391
Thermal correction to Enthalpy= 1.034335
Thermal correction to Gibbs Free Energy= 0.873709
Sum of electronic and zero-point Energies= -4050.221870
Sum of electronic and thermal Energies= -4050.160759
Sum of electronic and thermal Enthalpies= -4050.159815
Sum of electronic and thermal Free Energies= -4050.320441

C	2.05017000	3.20448400	1.81412700
C	2.07524100	2.04770900	1.01768100
C	2.71762600	2.07398600	-0.24292800
C	3.28308500	3.27646600	-0.67654200
C	3.25178000	4.42733400	0.11360600
C	2.63533100	4.38596700	1.36478000
H	1.56270400	3.15155600	2.78279000
H	3.74944100	3.29509100	-1.65558800
H	3.70436000	5.34680500	-0.24750500
H	2.60497600	5.27301000	1.99259100
C	2.71290100	0.83724000	-1.13361500
C	3.32519600	-0.42907800	-0.49158300
H	3.41500700	-0.30020100	0.58966400
C	2.60947000	-1.75905200	-0.75863900
C	1.20886900	-1.95883400	-0.62602400
C	3.42143000	-2.87828600	-1.00243500
C	0.70676800	-3.27228400	-0.70327200
C	2.90773000	-4.16740700	-1.11318800
H	4.48894700	-2.71120500	-1.09343600
C	1.53692100	-4.36154900	-0.94921100
H	-0.35568700	-3.41545200	-0.56796300
H	3.57153900	-5.00572300	-1.30660500
H	1.10943600	-5.36037700	-1.00301700
O	4.66435900	-0.41723100	-0.99628000
O	3.48408700	1.02726900	-2.32026800
H	1.69444200	0.61750500	-1.44739400
O	1.50821100	0.91751600	1.47251800
O	0.34654100	-0.92121600	-0.38682900
C	4.70698400	0.28269500	-2.23902200
C	4.75716500	-0.67397600	-3.43251500
H	5.66953300	-1.27861700	-3.39936300
H	3.89084000	-1.33926800	-3.42161600
H	4.75023500	-0.10344700	-4.36723400
C	5.91254300	1.22051700	-2.19928100
H	5.95561400	1.82292800	-3.11253100
H	5.84082100	1.88367300	-1.33387000
H	6.83767400	0.64015800	-2.12066200
Ti	0.10930000	-0.27575000	1.69923300
Ti	-1.77825200	-0.67555400	-0.76130900
O	0.98105300	-1.62894700	2.44938900
O	-1.13727700	1.09519300	0.35164700
C	-0.84462900	1.85252100	-0.63988000
H	0.15009200	1.79713300	-1.07720700
C	2.10861100	-2.41516200	2.80144500
H	2.66235600	-2.62364400	1.87661200
C	1.62620300	-3.73980200	3.39228700
H	1.05282700	-3.56741200	4.31076600
H	0.98811600	-4.26404500	2.67456500
H	2.47961200	-4.38468200	3.63247300
C	3.00869500	-1.63050100	3.75802500
H	2.48948100	-1.43187200	4.70292100
H	3.91935200	-2.19983700	3.97805900
H	3.29689400	-0.67259300	3.31433600
C	-1.58752300	3.10381700	-0.85382500
C	-2.73937900	3.39228300	-0.10314500
C	-1.10131700	4.04820400	-1.77226400
C	-3.39878100	4.60513800	-0.28185700
H	-3.08928100	2.66242000	0.61924700
C	-1.76579200	5.25929100	-1.94949000
H	-0.19615100	3.83333400	-2.33418600
C	-2.91611000	5.53740900	-1.20668400
H	-4.28626700	4.83037100	0.30313000
H	-1.38401400	5.98854200	-2.65823300
H	-3.43228000	6.48418800	-1.34140300
O	-3.48038400	-0.15802900	-0.80659100
O	-1.89496600	-2.17383000	-1.73631000
O	-0.70031900	0.50244700	3.13155200
C	-1.38869100	0.65026100	-2.66944600
H	-1.90152900	1.59515600	-2.84595700
H	-2.09050000	-0.12043200	-3.01652700
C	-0.08419200	0.55273200	-3.44969400
H	0.45451200	-0.37857500	-3.24765500
H	-0.27262800	0.59218300	-4.53367600
H	0.60533500	1.37616100	-3.23034900
C	-0.27790800	0.97039700	4.40196500
H	0.80794500	1.15178100	4.36692100
C	-0.56139500	-0.09510400	5.46343800
H	-0.06625900	-1.03450500	5.19926300
H	-0.19720300	0.22644500	6.44670200
H	-1.63915300	-0.28181800	5.53835800

C	-0.98370400	2.29359700	4.70565000
H	-0.77134500	3.03053000	3.92429000
H	-2.06898600	2.14489700	4.74887700
H	-0.65138600	2.70039300	5.66851200
C	-4.84114500	0.18312400	-0.97535900
H	-5.14705200	0.73892800	-0.07564800
C	-5.69596900	-1.08252300	-1.07980400
H	-6.75838600	-0.81858200	-1.13711800
H	-5.43351300	-1.65167700	-1.97877300
H	-5.54886800	-1.72665900	-0.20771000
C	-5.01265700	1.09512300	-2.19212600
H	-4.39873300	1.99418000	-2.09244600
H	-4.71970500	0.57344600	-3.11017200
H	-6.06116800	1.40010100	-2.28880100
C	-2.50466000	-2.90103400	-2.78825600
H	-3.30523200	-2.27276700	-3.21323700
C	-3.13210200	-4.18246500	-2.23633000
H	-3.87671800	-3.95397500	-1.46818000
H	-3.62478500	-4.74167800	-3.04026600
H	-2.36325500	-4.82360400	-1.79157500
C	-1.46892000	-3.18693300	-3.87840100
H	-1.04324200	-2.25520600	-4.26276600
H	-0.65128800	-3.79378200	-3.47622400
H	-1.93192300	-3.72636000	-4.71311700
C	-2.52357200	-1.81957700	2.13989500
H	-1.91446800	-1.99970300	3.03380600
C	-3.63757600	-0.84263900	2.51243900
H	-4.28557000	-0.64318200	1.65472600
H	-4.25166600	-1.26223500	3.31907300
H	-3.20309100	0.09921200	2.85455600
C	-3.04965400	-3.16430700	1.64153400
H	-3.67723000	-3.03591500	0.75319300
H	-2.22043900	-3.83007900	1.38263000
H	-3.65289700	-3.64776500	2.41939300
O	-1.62699400	-1.25608100	1.16665700

Diethyl zinc addition with Ti Pro-S precomplex

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.971693 (Hartree/Particle)
Thermal correction to Energy= 1.034000
Thermal correction to Enthalpy= 1.034944
Thermal correction to Gibbs Free Energy= 0.870448
Sum of electronic and zero-point Energies= -4050.255167
Sum of electronic and thermal Energies= -4050.192859
Sum of electronic and thermal Enthalpies= -4050.191915
Sum of electronic and thermal Free Energies= -4050.356411

C	-1.55511	-0.04113	-0.68921
H	-1.59489	0.76581	-1.44246
C	-0.87536	0.57335	0.63126
H	-1.65738	1.06588	1.22798
C	-3.01545	-0.45055	-0.40281
C	-3.9519	0.47151	0.09823
C	-3.45272	-1.76099	-0.64991
C	-5.26525	0.0897	0.36672
H	-3.65262	1.50258	0.27145
C	-4.77009	-2.15099	-0.37294
H	-2.76371	-2.46739	-1.10879
C	-5.67942	-1.22869	0.14129
H	-5.97079	0.82179	0.75221
H	-5.0838	-3.17162	-0.57934
H	-6.70346	-1.52471	0.3534
C	0.17815	1.62955	0.27373
C	1.55898	1.30867	0.29302
C	-0.24853	2.92259	-0.07967
C	2.4639	2.32951	-0.06302
H	2.18831	0.01526	0.49895
C	0.67502	3.90855	-0.42316
H	-1.31141	3.16246	-0.07703
C	2.04299	3.61327	-0.41651
H	3.53379	2.11703	-0.0613
H	0.33176	4.90583	-0.68926
H	2.76791	4.38076	-0.68029
O	-0.30009	-0.50513	1.35435
O	-0.78667	-1.12411	-1.12451
Li	0.86249	-0.82479	-0.36194
Li	-1.16228	-1.94513	0.54561
C	2.83905	-1.31625	0.71321
H	2.37002	-2.23794	0.31108
H	3.01477	-1.55278	1.78308
C	4.1967	-1.10701	0.02498
H	4.70058	-0.23734	0.47579
H	4.03174	-0.83483	-1.03095
C	5.16146	-2.30373	0.06875
H	4.67192	-3.17492	-0.39152
H	5.34636	-2.57732	1.11816
C	6.49728	-2.03995	-0.63389
H	7.02789	-1.19474	-0.17629
H	7.16069	-2.91237	-0.58402
H	6.34744	-1.79925	-1.69453
Li	1.34668	-0.13098	2.01786

Diethyl zinc addition with Ti Pro-S Product

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.971693 (Hartree/Particle)
Thermal correction to Energy= 1.034000
Thermal correction to Enthalpy= 1.034944
Thermal correction to Gibbs Free Energy= 0.870448
Sum of electronic and zero-point Energies= -4050.255167
Sum of electronic and thermal Energies= -4050.192859
Sum of electronic and thermal Enthalpies= -4050.191915
Sum of electronic and thermal Free Energies= -4050.356411

C	-1.55511	-0.04113	-0.68921
H	-1.59489	0.76581	-1.44246
C	-0.87536	0.57335	0.63126
H	-1.65738	1.06588	1.22798
C	-3.01545	-0.45055	-0.40281
C	-3.9519	0.47151	0.09823
C	-3.45272	-1.76099	-0.64991
C	-5.26525	0.0897	0.36672
H	-3.65262	1.50258	0.27145
C	-4.77009	-2.15099	-0.37294
H	-2.76371	-2.46739	-1.10879
C	-5.67942	-1.22869	0.14129
H	-5.97079	0.82179	0.75221
H	-5.0838	-3.17162	-0.57934
H	-6.70346	-1.52471	0.3534
C	0.17815	1.62955	0.27373
C	1.55898	1.30867	0.29302
C	-0.24853	2.92259	-0.07967
C	2.4639	2.32951	-0.06302
H	2.18831	0.01526	0.49895
C	0.67502	3.90855	-0.42316
H	-1.31141	3.16246	-0.07703
C	2.04299	3.61327	-0.41651
H	3.53379	2.11703	-0.0613
H	0.33176	4.90583	-0.68926
H	2.76791	4.38076	-0.68029
O	-0.30009	-0.50513	1.35435
O	-0.78667	-1.12411	-1.12451
Li	0.86249	-0.82479	-0.36194
Li	-1.16228	-1.94513	0.54561
C	2.83905	-1.31625	0.71321
H	2.37002	-2.23794	0.31108
H	3.01477	-1.55278	1.78308
C	4.1967	-1.10701	0.02498
H	4.70058	-0.23734	0.47579
H	4.03174	-0.83483	-1.03095
C	5.16146	-2.30373	0.06875
H	4.67192	-3.17492	-0.39152
H	5.34636	-2.57732	1.11816
C	6.49728	-2.03995	-0.63389
H	7.02789	-1.19474	-0.17629
H	7.16069	-2.91237	-0.58402
H	6.34744	-1.79925	-1.69453
Li	1.34668	-0.13098	2.01786

25a

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.283942 (Hartree/Particle)
Thermal correction to Energy= 0.302229
Thermal correction to Enthalpy= 0.303173
Thermal correction to Gibbs Free Energy= 0.238450
Sum of electronic and zero-point Energies= -784.534571
Sum of electronic and thermal Energies= -784.516284
Sum of electronic and thermal Enthalpies= -784.515340
Sum of electronic and thermal Free Energies= -784.580063

C	-4.00602000	-0.14345100	-0.85134200
C	-2.70975400	-0.59485500	-0.53795700
C	-1.93752800	0.31999400	0.22583800
C	-2.41397500	1.57077200	0.64944600
C	-3.70358400	1.96928100	0.29939700
C	-4.50052400	1.10494500	-0.45526100
H	-4.66953900	-0.78523600	-1.43388800
H	-1.78542400	2.23266100	1.24650900

H	-4.08393100	2.93670200	0.61874500
H	-5.51081400	1.40595000	-0.72925600
C	-0.50834100	-0.04965000	0.59458000
C	0.50831000	-0.05057600	-0.59495200
H	0.10763100	0.62088000	-1.36165000
C	1.93750100	0.31968200	-0.22668100
C	2.70976800	-0.59412100	0.53836600
C	2.41380100	1.57002200	-0.65171600
C	4.00579700	-0.14201500	0.85166900
C	3.70323600	1.96922600	-0.30180300
H	1.78526300	2.23105100	-1.24974300
C	4.50013600	1.10601200	0.45419500
H	4.66928200	-0.78292600	1.43521700
H	4.08347500	2.93633000	-0.62224300
H	5.51026100	1.40760100	0.72815400
H	-0.10764400	0.62289300	1.36032100
Li	-1.34928100	-2.03663600	-0.66826200
Li	1.34919800	-2.03558200	0.67050100
O	-0.44890400	-1.42741100	1.15303300
O	0.44897300	-1.42915000	-1.15116900
C	-1.07737200	-1.53406800	2.44137400
H	-2.11447700	-1.19530100	2.37813200
H	-1.04420800	-2.58871500	2.72628700
H	-0.52641200	-0.93455400	3.17500100
C	1.07822700	-1.53855200	-2.43883600
H	2.11572500	-1.20101500	-2.37535900
H	1.04384900	-2.59359900	-2.72196800
H	0.52859500	-0.93944400	-3.17379000

25b

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opt=calcfc freq=noraman b3lyp/6-31g(d)

Zero-point correction= 0.290107 (Hartree/Particle)
Thermal correction to Energy= 0.307961
Thermal correction to Enthalpy= 0.308905
Thermal correction to Gibbs Free Energy= 0.246182
Sum of electronic and zero-point Energies= -822.662912
Sum of electronic and thermal Energies= -822.645058
Sum of electronic and thermal Enthalpies= -822.644114
Sum of electronic and thermal Free Energies= -822.706838

C	-2.67595200	-1.94988200	0.86318800
C	-1.59425400	-1.07464900	1.13660500
C	-0.35654200	-1.48507900	0.55281200
C	-0.21801300	-2.64183500	-0.23433000
C	-1.33411600	-3.44835500	-0.49725400
C	-2.57272200	-3.09995000	0.05794500
H	-3.66407700	-1.71262300	1.26120100
H	0.75234500	-2.89271400	-0.65571500
H	-1.23579800	-4.33552300	-1.11745000
H	-3.44734400	-3.71806700	-0.13659400
C	0.77870500	-0.49056100	0.60080300
C	0.77873000	0.49003300	-0.60119000
H	0.69511000	-0.09951800	-1.52744800
C	-0.35610200	1.48501900	-0.55300500
C	-1.59403300	1.07526300	-1.13681800
C	-0.21702300	2.64149900	0.23445500
C	-2.67530600	1.95097900	-0.86327000
C	-1.33275100	3.44848200	0.49758100
H	0.75345800	2.89178800	0.65592500
C	-2.57152200	3.10080500	-0.05774700
H	-3.66354300	1.71427600	-1.26132800
H	-1.23403300	4.33543700	1.11801900
H	-3.44584600	3.71929900	0.13693300
O	2.08506200	1.04560400	-0.48929000
O	2.08485000	-1.04652500	0.48844700
H	0.69557000	0.09896100	1.52710100
C	2.94655700	-0.00038300	0.00001500
C	3.78588600	0.57453700	1.13666300
H	4.36830400	1.43070800	0.78129800
H	3.13686100	0.90927800	1.95124600
H	4.47324300	-0.18406400	1.52391800
C	3.78711300	-0.57501900	-1.13584300
H	4.36960300	-1.43091400	-0.77993700
H	3.13892800	-0.91005800	-1.95096300
H	4.47446900	0.18387500	-1.52251600
Li	-1.83320500	-1.00542900	-1.16557800
Li	-1.83295500	1.00602700	1.16537900